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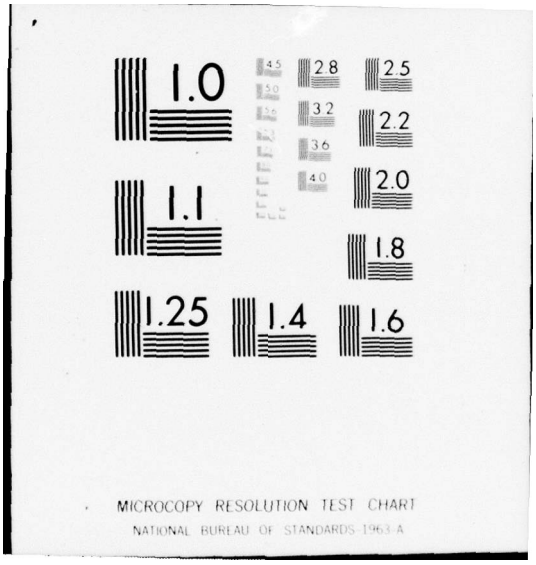
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DEVELOPMENT OF HIGH PRESSURE LIQUID CHROMATOGRAPHIC TECHNIQUES

ERIC H. WANG CIVIL ENGINEERING RESEARCH FACILITY
UNIVERSITY OF NEW MEXICO

OCTOBER 1976

FINAL REPORT : DECEMBER 1975 - JUNE 1976

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Development of high pressure liquid chromatography detectors is discussed. Preliminary evaluation of a beta-induced luminescence detector employing a tritium source and operated in a luminescence quenching mode is presented. An ultrasonic velocity detector is described, along with calibration data, complete construction details, and operating instructions. A solid-state electrode for silver ion detection using a $Ag_6I_4WO_4$ pellet is described, and calibration data and interference studies are presented. Construction of a beta-induced luminescence detector to be operated in a direct luminescence mode is described. Data for the

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recovery and preliminary characterization of refractory organics from treated wastewater using an organics-carbon minifilter are presented. The carbon chloroform extract of the minisampler is analyzed using high pressure liquid chromatography, and column parameters providing maximum resolution of components are given in detail.

PREFACE

This report documents work performed during the period 1 December 1975 through 30 June 1976 by the University of New Mexico under contract F29601-76-C-0015 with the Air Force Civil Engineering Center, Air Force Systems Command, Tyndall Air Force Base, Florida 32403. Major Michael G. MacNaughton, AFCEC/EVC managed the program for the Center.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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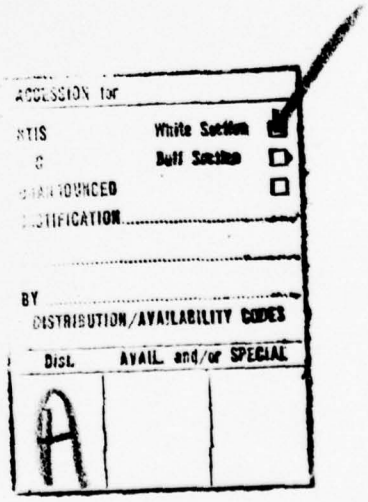

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SECTION I

INTRODUCTION

BACKGROUND

As a result of its extensive maintenance activities, the Air Force discharges waste materials which contain both metals and organics. Although total metals analysis is possible by atomic absorption and other instrumental and wet chemical techniques, the actual speciation of the compounds is unobtainable at present.

Knowledge concerning the types and concentrations of trace organics and metals in natural waters has become exceedingly more important in recent years as more data are gathered on their effect on humans, aquatic organisms, and plants. Organics and organometallics, even at the parts-per-billion level, have been shown to exert a significant biotoxic and phytotoxic effect in fresh and marine waters.

Analyzing trace organics and metal organic complexes in the environment without disturbing the natural equilibrium is not possible with the present technology. Virtually all present techniques involve indirect measures of the speciation of the different elements (measurement by specific ion electrodes being a notable exception). Extraction with organic solvents has been the most prevalent method of separating inorganic and organically bound metals into their separate fractions. This technique, although applicable for gross differentiation of these two components, does not give the actual species which exist in either fraction. Analysis by gas chromatography is useful only for volatile compounds. Anodic stripping voltametry, an electrochemical technique, is also useful for determining a limited number of complexed metals but it gives only limited data about complex solutions containing organics and metals in both the free and complex forms.

High Pressure Liquid Chromatography (HPLC) is a relatively new technique which has tremendous potential for analysis and identification of aqueous

pollutants. With gas chromatography, the compounds need to be volatile; with HPLC this is not necessary. Neither is it necessary to perform extractions of the solutions; both metals and organics can be analyzed at the same time. Although HPLC is beginning to be used more extensively, particularly in the analysis of drugs, to date there have been few uses of this technique for the identification and measurement of pollutants.

One of the most serious shortcomings of HPLC is the lack of detectors which would measure elution peaks from the liquid chromatograph with the same broad applicability as does the flame ionization detector in gas chromatography. The most common detectors available are the ultraviolet-absorption and the refractive-index detectors. The ultraviolet-absorption detectors, which usually operate at the mercury lines at 253.7 and 280 mm, are useful only for those compounds containing chromophores which absorb at these wavelengths. The refractive-index detector lacks the sensitivity of the ultraviolet-absorption detector and also exhibits a strong temperature dependence. To make HPLC more generally applicable in routine analysis requires detectors which are general in their response to numerous elements or compounds.

Collection of samples for analysis of organics from aqueous samples such as natural waters or treated effluents is made difficult by the low levels of organics and metals as aquo ions or complex ions. Many investigators have successfully employed the Organics-Carbon Adsorbable Minifilter Procedure to concentrate refractory compounds in natural and finished waters for further analytical characterization and as an effluent quality parameter. Many investigators feel that because of the varying toxicity of organic contaminants, specific organic compounds should be monitored. However, with the current state of organic analysis, this is not possible. The best alternative is to determine a suitable organic parameter which includes a broad spectrum of organic compounds and assume that the level of this parameter is related to the level of toxicity of the water. The amount of carbon chloroform extract (CCE) obtained by the Organics-Carbon Adsorbable Minifilter Method was included in proposed drinking water regulations. Also, a method for the concentration and fractionation of refractory organics from both water and treatment-system wastewater to obtain environmentally significant compounds is desirable in order to determine the most appropriate application of advance-technology detection systems.

OBJECTIVES

The objectives of this research and development were as follows: (1) to develop HPLC techniques for the identification and measurement of organics and metals in natural waters, including the design and use of new detectors for HPLC; (2) to evaluate the ability of pulsed and impulsed carbon beds and solvent extraction to recover refractory materials from secondary wastewater-treatment facilities; (3) to characterize waste effluents by conventional parameters; and (4) to characterize and identify selected fractions of the wastewater concentrates.

SCOPE

Procedures for the use of HPLC for analysis of wastewater concentrates developed as water samples were made available. Further work on the beta-induced luminescence detector, operating in the luminescing quenching mode, was performed; circuit modifications to the ultrasonic velocity detector were completed and calibration studies were initiated; and fabrication techniques, calibration studies, and response characteristics of the electrochemical silver-ion detector were completed.

Five CCEs were recovered from the effluent of a secondary treatment plant. The ability of the activated carbon to adsorb the nonvolatile total organic carbon in low-turbidity, secondary effluents was determined. Preliminary fractionation of the organics by HPLC with selected eluants was also accomplished.

SECTION II
LITERATURE REVIEW

Literature surveys taken from *Chemical Abstracts* for the period 1 January 1969 to 20 October 1975 have been presented in two previous reports (References 1 and 2). The complete literature searches themselves are available at the University of New Mexico Library under the title *Column Chromatography, RS-481.* However, since these literature searches did not yield much information on the use of ion-selective electrodes as column detectors or on their direct use for water analysis, the reader is referred to the more recent literature surveys published in *Analytical Chemistry*, which contains references to numerous applications of ion-selective electrodes to water analyses. (References 3, 4, 5). The following brief literature review is indicative of the work now being done in the ion-selective electrode area.

The general use of ion-selective electrodes has been discussed by many workers. Maienthal and Taylor (Ref. 6) have discussed the application of electrochemical techniques, including ion-selective electrodes, to water analysis. Several workers have discussed the application of chemical sensing electrode analysis (References 7, 8, 9) and Kempf and Sonneborn have compared atomic-absorption, dithizone-photometry, and ion-selective electrode methods for water analysis (Reference 10). The determination of copper, mercury (II), sulfate, sulfides, calcium, and magnesium in waters has been facilitated by ion-selective electrodes (References 11 through 19). Ion-selective electrode analysis for ammonia in waters and wastes has been the subject of numerous investigations (References 20 through 27) as well as the analysis for nitrate (References 28, 29, 30). Ion-selective, potentiometric sensors have been adapted for use as detectors in liquid chromatography (Reference 31), and new designs for coulometric and amperometric detectors used in liquid chromatography have also been the subject of recent investigations (References 32, 33, 34).

SECTION III
DETECTOR DEVELOPMENT

BETA-INDUCED LUMINESCENCE DETECTOR

The second-generation beta-induced luminescence detector described previously by Walters (reference 1) and Caton and Walters (reference 2) was connected to the end of a column which was attached to the Varian 4100 HPLC. Since previous work indicated that this detector is best utilized in conjunction with a highly luminescent solvent with subsequent monitoring of the quenched luminescence caused by the solutes being detected, an eluant solvent consisting of 0.50 g of $(CH_3)_2$POPOP and 5.0 g of PPO in 1 ℓ of xylene was used.

The eluant solvent was degassed and pumped through a 25-cm C-10 Micropak column. After the detector output became steady, individual samples of CH_2Cl_2, $CHCl_3$, CCl_4, C_2H_5OH, $C_6H_5NO_2$, and C_6H_5Br were injected at the top of the column. Decreased luminescence was observed with all samples, except C_2H_5OH, as they emerged from the column. Assorted mixtures of the remaining five compounds were injected, and quenched luminescence was again observed; however, the components were not separated by the column. Although each of the solutes should have a different elution time under normal separation conditions, all had identical elution times with scintillation mixture as an eluant. This was undoubtedly the result of saturation of the column by the PPO and/or $(CH)_2$POPOP and subsequent exclusion of the injected samples.

Two methods for introducing the scintillator at a point between the column and the detector were considered. The first consisted of attaching an after column containing a dry mixture of PPO/$(CH_3)_2$POPOP in the weight proportions of 10:1, with the hope that the scintillator mixture would dissolve at a constant rate into the xylene eluant solvent after the samples were separated. The second consisted of pumping a scintillator solution into the eluant between the separation column and the detector.

In the first case, a 5-mm-inside-diameter, 17.2-cm-long column (3.4-mℓ volume) was packed with the dry scintillator mixture and mounted between the

separation column and the detector. As pure xylene was pumped through the chromatographic system, the detector recorded strong light levels; i.e., the dry scintillator mixture was dissolving as planned. Injection of the sample mixtures yielded broad, unresolved peaks. Some mixing in the post column should have decreased the resolution; however, the effect was greater than that expected.

In the second case, the scintillator solution was introduced into the system as follows: A Swagelock SS-100-3 union tee was connected to the C-10 Micropak column and the tee was connected to a Varian low-pressure pump filled with the scintillator mixture at twice the normal concentration; the third connection was made to the detector. By employing equal column-solvent (pure xylene) and scintillator-mixture flow rates, the solution entering the detector would be a scintillator mixture of normal concentration. This method would also keep the post column dead volume to a minimum and thus reduce post-separation mixing. Unfortunately, this technique failed since it was not possible to simultaneously regulate the flow rates of the high-pressure and low-pressure pumps. The high-pressure pump delivers a constant flow by maintaining whatever pressure is required to produce the desired flow rate. The low-pressure pump cannot do this; it did not deliver the scintillator mixture at a steady rate. Thus, the scintillator concentration introduced into the detector varied in an erratic manner, resulting in erratic detector output which completely masked any detection of solutes eluted through the separation column. It is believed that this problem could be eliminated if a second high-pressure pump were used to provide a steady and reproducible flow of scintillator mixture into a small chamber in which eluted solutes and scintillator could be uniformly mixed before they entered the detector. Since a second high-pressure pump was not available and could not be obtained, this approach was abandoned.

VARIABLE-PATH-LENGTH, BETA-INDUCED LUMINESCENCE DETECTOR

Construction of the variable-path-length, beta-induced luminescence detector described in detail in Reference 2 was completed. The screw mount to contain the 300-mCu tritium source was sent to Sandia Laboratories for vapor deposition

of a titanium layer on the surface, followed by conversion of a portion of the titanium layer to titanium tritide (Ti^3H_2).

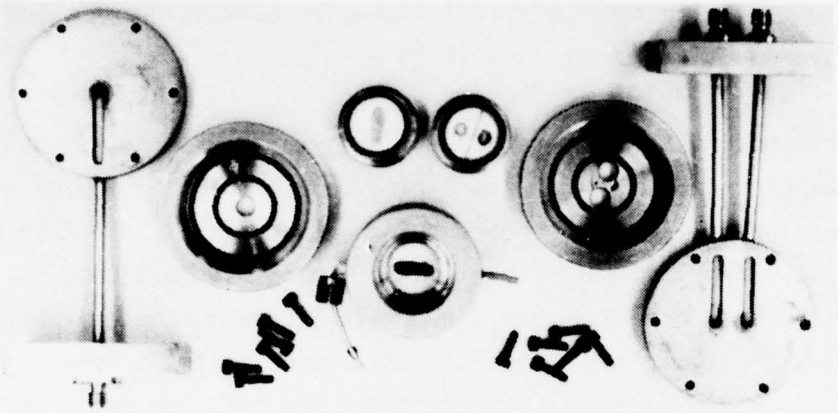
Several minor modifications were made to the variable-path-length, beta-induced luminescence detector. The O-ring in the original design was replaced by a compression spring with a compression rating of 7.7 to 9.2 lb at the two extremes. The inlet and outlet ports were remachined to accept Swagelock fittings; as modified, they now have a 0.007-in (inside diameter) capillary tube and a thin-walled tube, respectively. After modifications were completed, a nonradioactive screw mount was installed and the detector was examined for leaks. Leaks occurred at the interface of the quartz lens and the stainless-steel lens mount. A Teflon cup was machined to hold the lens and the lens was then inserted into the detector. Dow Corning RTV-732 sealant was applied in thin layers at surface interfaces where leaks might occur. The final assembly did not leak at flow rates of 6 mℓ/min (well in excess of HPLC operating conditions).

ULTRASONIC VELOCITY DETECTOR

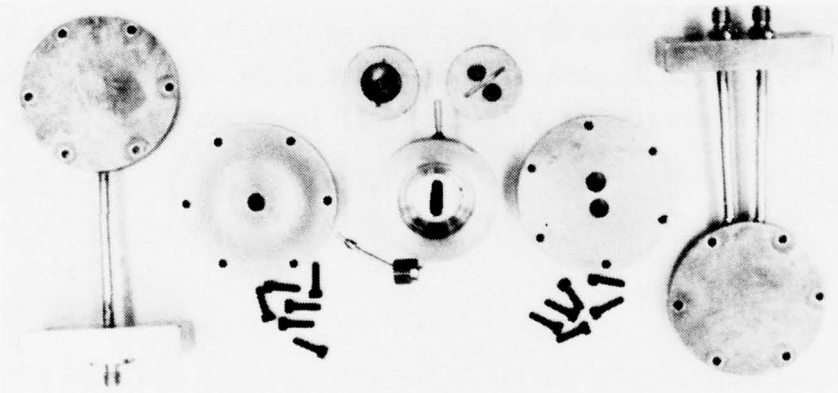
The theory and construction of the ultrasonic velocity detector (Figure 1) are described in References 1, 2, and 35. However, several minor modifications to the electronic circuits have been made to improve the performance of the detector. These modifications are discussed below. The circuit diagrams for all electronic modules, operating instructions, and a list of those components which must be obtained from specific manufacturers are given in the Appendixes. All other electronic components and parts are standard and may be obtained from any source.

Modifications

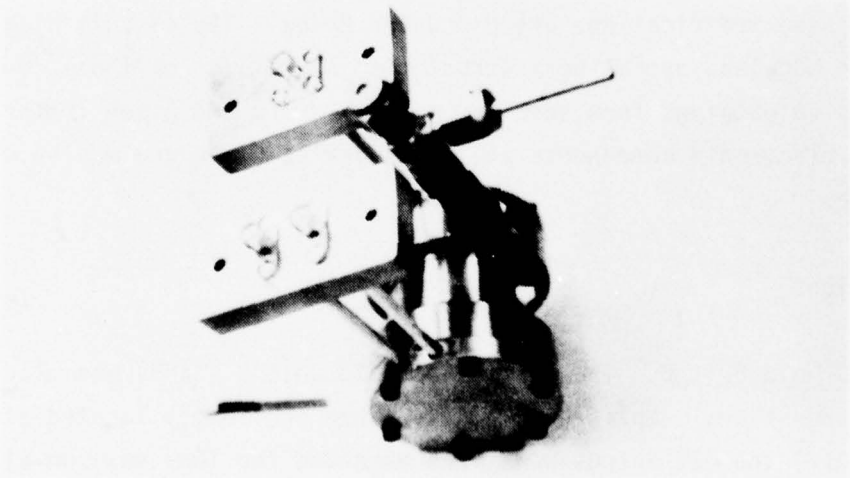
Sample-and-Hold Unit B. The sample-and-hold unit B (S&HB) was placed at the input to operational amplifier 4 (OA4). When previously located after the divider (DIV) the DIV output sometimes exceeded the 10-V maximum allowable input to S&HB. As presently located, the input to S&HB never exceeds 3.6 V. To obtain exact unity gain from OA1 and OA2, it was necessary to use



Front View of Disassembled Detector Cell



Back View of Disassembled Detector Cell



Fully Assembled Detector Cell

Figure 1. Ultrasonic Velocity Detector

trimming potentiometers on the feedback and/or input resistors for these amplifiers. The values of these trimming potentiometers changed from time to time; thus, frequent adjustment to provide the unity gain was necessary. The best results were finally obtained by eliminating the trimming potentiometers and trimming resistors RA, RB, RC, RD, and RE and placing large resistors (10 to 50 MΩ) parallel to resistors RA through RE. These parallel resistors had temperature characteristics similar to those of resistors RA through RE, and their use resulted in drift-free performance of OA1 and OA2.

1-MHz Oscillator. The logic out circuit was eliminated. After modifications on the logic circuit, the 1-MHz signal was no longer required by the logic circuit.

Logic Circuit. Since the 1-MHz signal was no longer required, pin 5 of $IC1_2$ is now maintained at 5 V. The end of conversion pulse is now generated at pin 2 of IC6 instead of at the digital panel meter (DPM). With this modification, the constant cycle period is maintained and is not affected by the converting time of the DPM.

Local Oscillator. The local oscillator (a commercially available signal generator) was too drift prone. Hence, a more stable oscillator which generates a 1.010000- or 1.005700-MHz sine wave was built.

Recorder Offset. A simple voltage offset is now being used before the strip chart recorder to balance the detector system output.

Detector Cell. Modifications to the detector cell itself have been minor. The cell volume was reduced to obtain higher sensitivity by filling up a portion of the cell with Dow Corning RTV-732 sealant, without restricting the flow of liquid through the cell. When in use, the detector cell should be placed in a constant-temperature bath which provides ± 0.02° C control. Otherwise, temperature fluctuations will cause considerable baseline drift when the output of the detector system is recorded.

Performance Studies

Studies of detector performance were made after all the modifications were

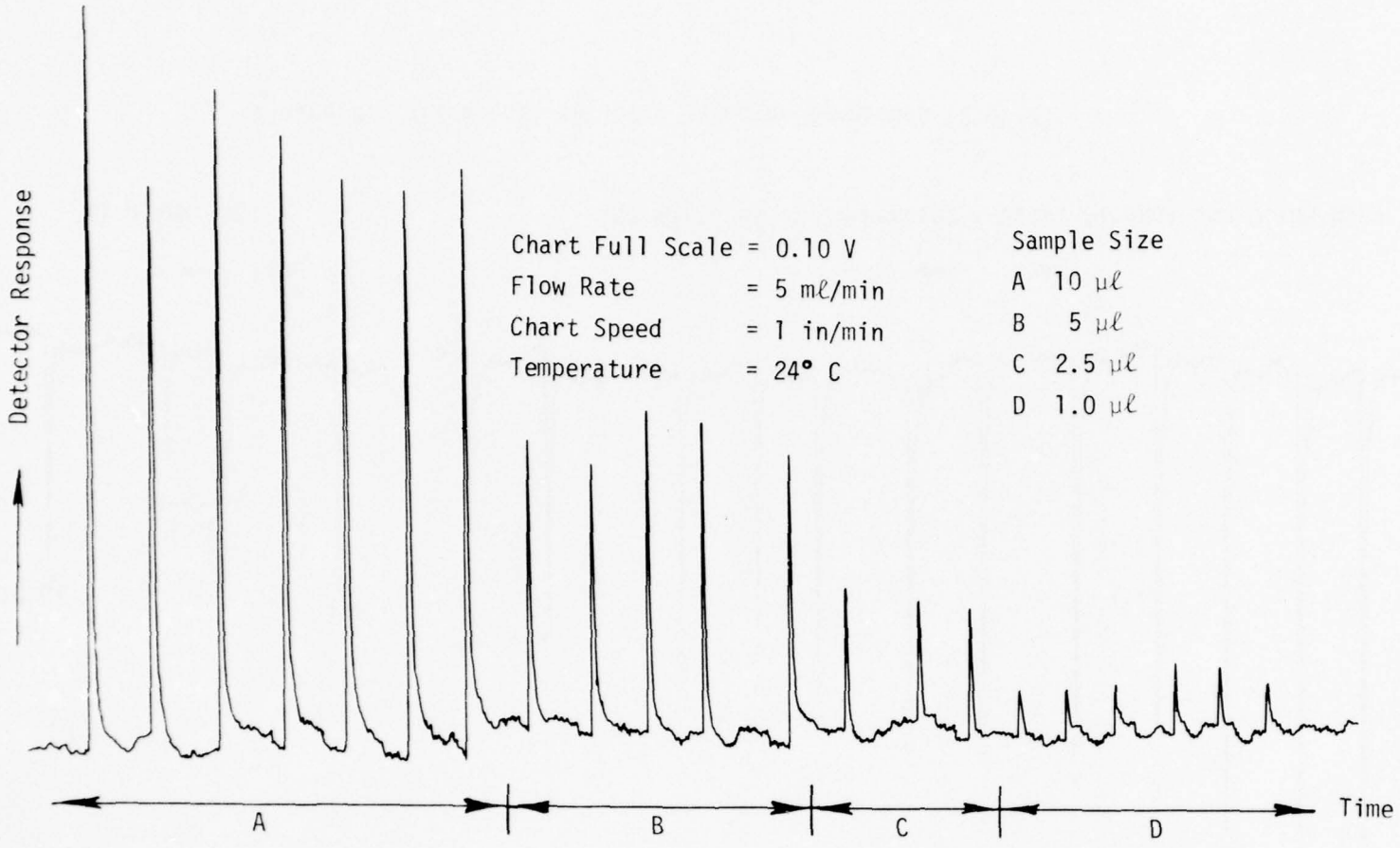
completed. Data were obtained, without using a separation column, by injecting samples directly into a stream of solvent before the latter entered the detector cell. A 10-μℓ syringe with a 5-cm-long needle was used to inject various amounts of the sample at a point about 3 cm before the cell. Solvent flow was maintained by gravity, and both the cell and the solvent reservoir were maintained at the same temperature by a temperature bath controlled to within ± 0.01°C. The detector cell was operated in a single transducer mode; i.e., the difference signal between two transducers was not recorded during the runs.

Figure 2 (a) shows the detector's response to t-butyl alcohol (TBA) dissolved in water (20 percent TBA) as a function of various sample sizes. The temperature of all solutions, solvent, and detector cell was maintained at 24°C; the flow rate was 5 mℓ/min; and a recorder chart speed of 1 in/min was employed. The full-scale, recorder range was 100 mV. Figure 2 (b) shows the data obtained for 0.10M NaCl and Figure 2 (c) shows the data for mixtures of 20 percent TBA and 0.10M NaCl. In the latter case, the total response is essentially the sum of the responses to the individual components. Peak height reproducibility was fair; most of the variation was due to nonreproducible injection techniques. Nevertheless, the average peak height was closely proportional to the sample size, and the detector response was linear over the concentration ranges studied. The response sensitivity, signal-to-noise ratio, and baseline stability are so greatly improved (Figure 2) that data obtained earlier are not representative of the detector's performance. The sensitivity for TBA is better than 0.2 mg in Figure 2 (a); and if more amplification were used, the sensitivity could be improved by a factor of ten.

SOLID-STATE DETECTOR FOR SILVER ION

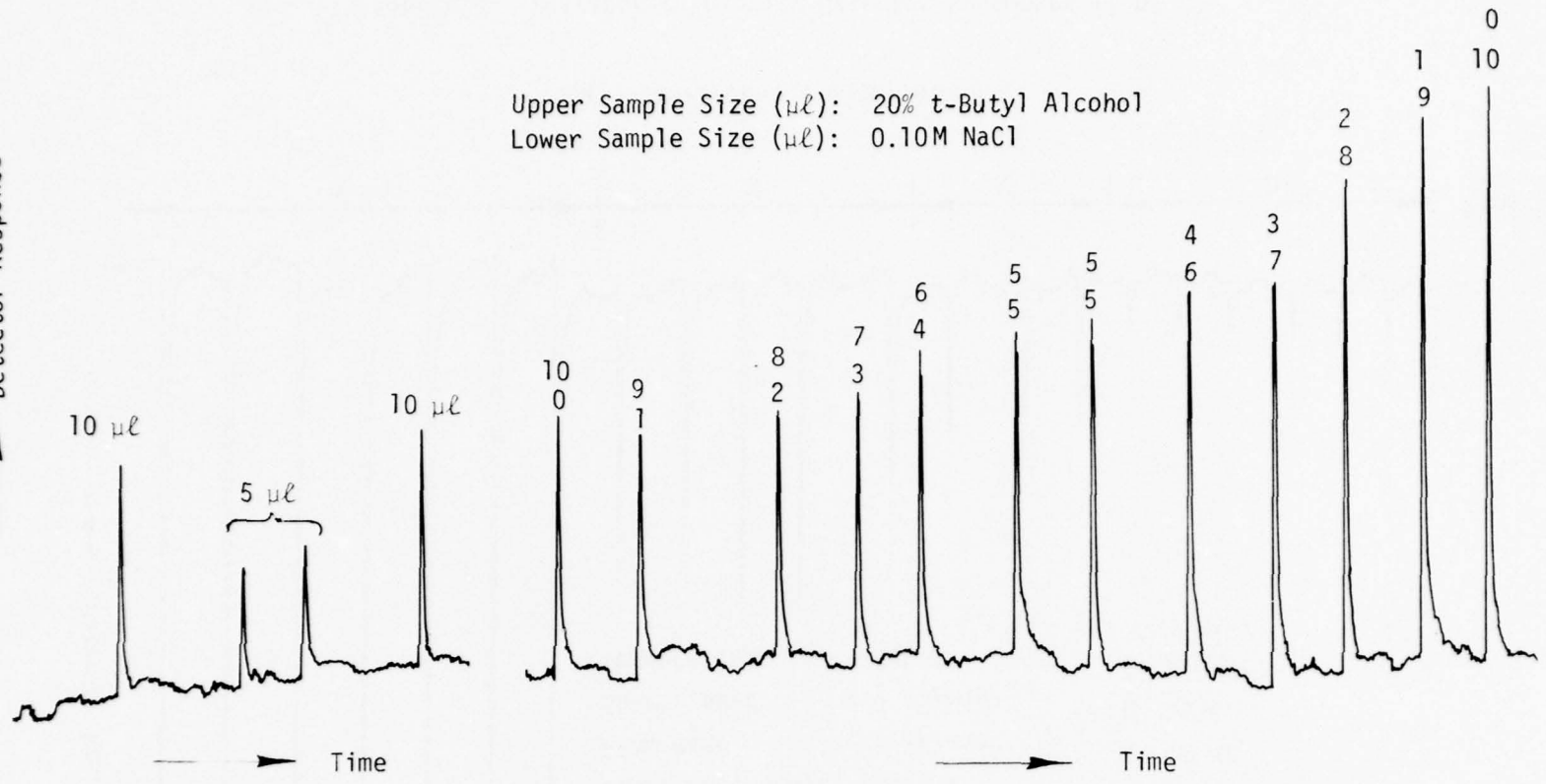
Introduction

Previous solid-state electrodes were constructed from $Ag_6I_4WO_4$ and $Ag_{19}I_{15}P_2O_7$. These materials were somewhat unsuccessful because they disintegrated after a few hours of use and the electrodes then gave poor responses. However, the stability was greatly increased by pressing the solid-state pellets at much higher pressures, and new electrodes were constructed from the new stabilized pellets.



(a) 20-Percent t-Butyl Alcohol

Figure 2. Ultrasonic Velocity Detector Responses (1 of 2)



(b) 0.10M NaCl

(c) Mixtures of 20-Percent t-Butyl Alcohol and 0.10M NaCl

Figure 2. Ultrasonic Velocity Detector Responses (2 of 2)

The pure samples of $Ag_6I_4WO_4$ and $Ag_{19}I_{15}P_2O_7$ were prepared as described in Reference 2 with the following minor changes in procedure. Freshly precipitated samples of AgI, $Ag_4P_2O_7$, and Ag_2WO_4 were carefully washed with very dilute nitric acid (1 percent or less) to free the precipitates of nonvolatile, adsorbed ions which may have been present in excess after precipitation. The precipitates were then washed with distilled water under photographic safe lights and dried overnight under a flow of dry nitrogen. The dried materials were then weighed and combined in the proper stoichiometric ratios, passed through a 100-mesh sieve, placed in Pyrex tubes, and pumped down to 10^{-4} torr for 4 hr. The tubes were sealed under vacuum and placed in a furnace at 250°C for 20 hr to melt the materials. After cooling, the materials were ground and stored in the dark.

The electrode materials were pressed into 0.25-in-diameter pellets, 0.5 to 2 mm thick, at pressures of both 43,000 and 120,000 psi. (Pellets used in the previous work had been pressed at 24,000 psi with an IR pellet press.) The electrodes were constructed according to the design shown in Reference 2. Glass tubing (about 0.25 in outside diameter) was ground flat on one end and the pellet was attached with Dow Corning RTV-732 silicone rubber sealant which was applied in a thin layer to the flat ground end. After the pellet had been mounted securely, a thin layer of the sealant was applied to the exposed edge of the pellet and to the glass at the point of pellet/tubing contact. Mercury was used as an internal contact to the pellet and a platinum wire lead was inserted to provide external contact with the mercury.

Electrodes constructed of both materials and pressed at the two pressures were tested for Nernstian response to silver ion in 0.1M KNO_3. The $Ag_6I_4WO_4$ electrodes showed responses superior to those made with $Ag_{19}I_{15}P_2O_7$; pellets pressed at 120,000 psi showed no advantage over those pressed at 43,000 psi. In fact, the pellets pressed at the higher pressure tended to be more fragile, and on occasion they spontaneously fractured or split in the plane parallel to the face of the pellet. The $Ag_{19}I_{15}P_2O_7$ electrode was not considered any further and emphasis was placed on establishing the characteristics of the $Ag_6I_4WO_4$ electrode.

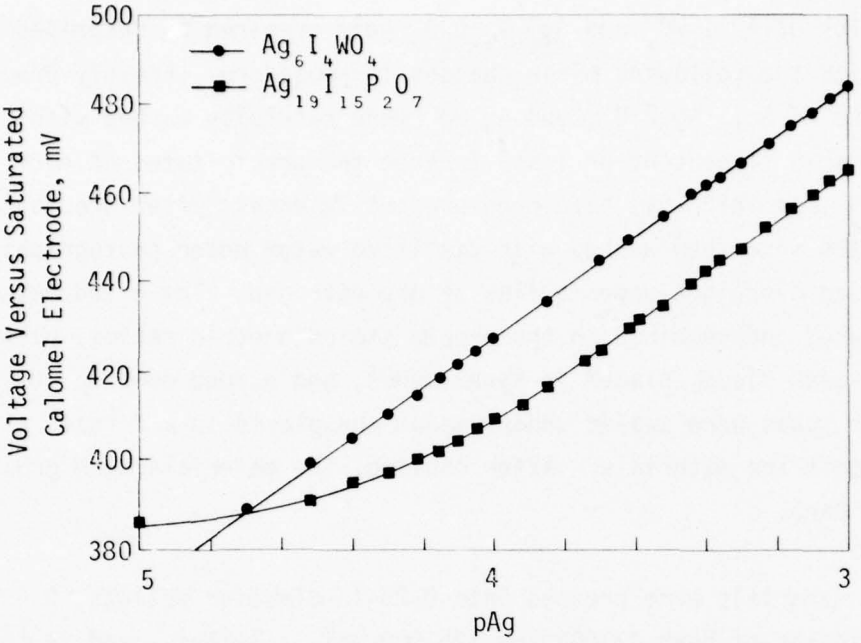


Figure 3. Solid-State Electrode Responses

Potentiometric Studies

All potentiometric studies were conducted with the $Ag_6I_4WO_4$ electrode described above dipped into 0.10M KNO_3 which contained various amounts of $AgNO_3$. The electrodes were rotated during use and voltage readings were made against a double-junction, reference electrode[1] with a reference voltage equal to that of the saturated calomel reference electrode. An Orion No. 94-16 silver/sulfide electrode was used as a comparison standard for work with the $Ag_6I_4WO_4$ electrodes.

A typical response for a rotated $Ag_6I_4WO_4$ electrode is shown in figure 3. An undesirable electrode such as the $Ag_{19}I_{15}P_2O_7$ electrode showed limited linear response (Figure 3). All $Ag_6I_4WO_4$ electrodes tested yielded linear responses for silver-ion concentrations down to at least 3×10^{-5}M, with slopes ranging from 56.7 to 58.1 mV/ten-fold change in silver-ion concentration. All of the

1. Model 90-02: Manufactured by Orion Research, Inc., 380 Putnam Avenue, Cambridge, Massachusetts 02139.

$Ag_6I_4WO_4$ electrodes deviated more from true Nernstian behavior than did the Orion electrode (Figure 4), but some of this deviation could possibly be attributed to electrode construction. The Orion electrode has a solid internal contact which makes the electrode more stable because it eliminates the internal solution/solid interface; the $Ag_6I_4WO_4$ electrode has a liquid mercury/solid interface and should be less noisy if a solid contact were used.

All electrodes, except those with obvious faults (i.e., cracks or leaks) were quite stable. They could be stored in solutions, in the light, or allowed to dry out for months without affecting their response. If response became sluggish, the electrode could be rejuvenated by polishing the surface of the pellet lightly and then soaking it in a 10^{-3}M $AgNO_3$ solution for a few minutes.

Interference Studies

Copper (II) and lead (II), the only metal cations studied, did not interfere with the $Ag_6I_4WO_4$ electrode response in 1.00×10^{-4}M $AgNO_3$ when present at concentrations 100 times the concentration of the silver ion. Substances which formed complexes or insoluble silver salts did seriously affect the

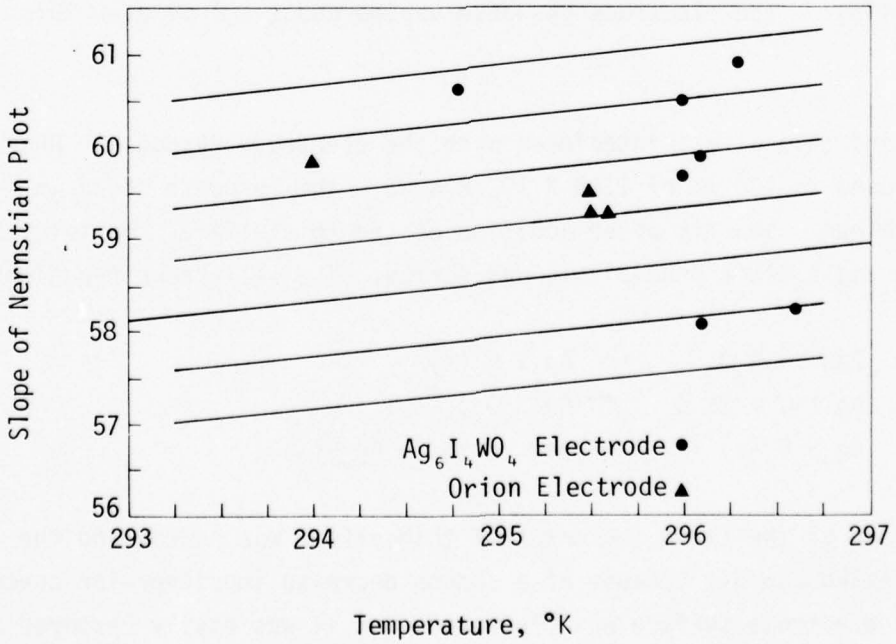


Figure 4. Summary of Response Studies on $Ag_6I_4WO_4$ Electrode

response of the electrodes, as would be expected for an electrode which responds to silver-ion activity.

Four new electrodes were selected at random and used to test electrode response to chloride, bromide, and iodide ions in the absence of silver nitrate. Increments of the separate sodium halides were added to 0.100M KNO_3 and the electrode responses were recorded. These results are shown in Figure 5. Linear plots of voltage versus log $[Ag^+]$ similar to those obtained with a silver metal electrode were obtained. When a silver metal electrode is used, however, parallel lines having the order Cl^-, Br^-, I^- are obtained. Figure 5 shows the order Cl^-, I^-, Br^- and the nearly identical response to iodide and bromide. Thus, the response plots are not in order of the solubility of the silver halides but are more likely in a sequence determined by the nature of the solid-state electrode itself. The response to the chloride ion is normal (Figure 5); i.e., the response to chloride is almost constant until the solubility product of silver chloride is exceeded at the surface of the electrode pellet.

The $Ag_6I_4WO_4$ electrode was insensitive to pH changes between a pH of 2 to 7 (pH range studied). The electrode response varied about ± 1 mV over this range.

Both ammonia and thiosulfate interfered with the electrode response. When $Na_2S_2O_3$ was added to 100 mℓ of 1.00×10^{-3}M $AgNO_3$, the response shown in Figure 6 was obtained. Shortly after addition of the thiosulfate, the solution became turbid and a black precipitate was formed. The well-known reactions

$$2Ag^+ + S_2O_3^{=} \longrightarrow Ag_2S_2O_3(s)$$
$$AgI(s) + 2S_2O_3^{=} \longrightarrow Ag(S_2O_3)_2^{\equiv} + I^-$$
$$Ag_2S_2O_3(s) + H_2O \longrightarrow H_2SO_4 + Ag_2S(s)$$

occurred as soon as the first increment of thiosulfate was added, and the response decreased rapidly because of a sudden decrease in silver-ion concentration. The electrode surface was blackened, but it was easily restored to its original condition by polishing. Addition of $Na_2S_2O_3$ to a silver-free solution of 0.100M KNO_3 produced the results shown in Figure 7. A precipitate,

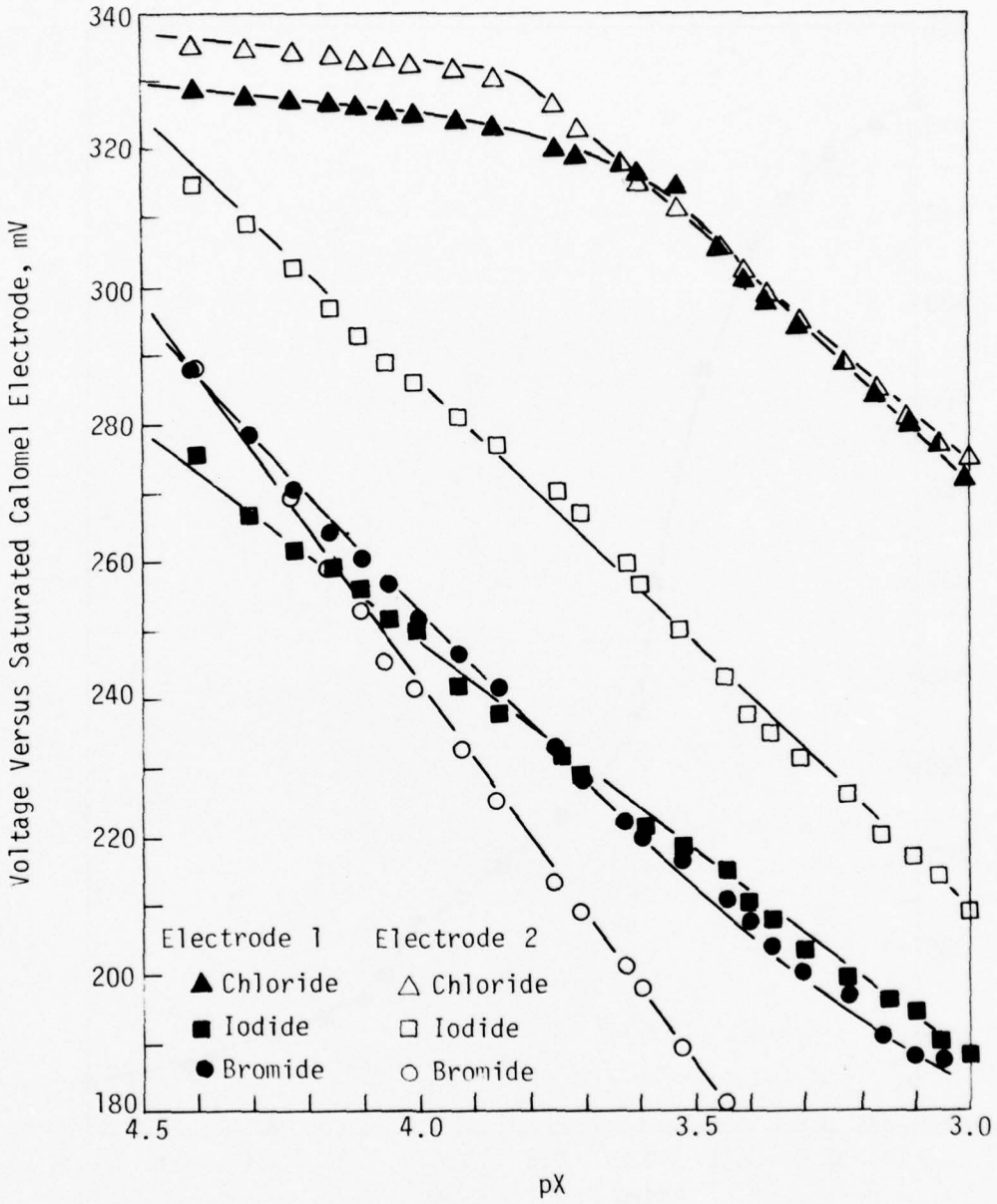


Figure 5. Response of $Ag_6I_4WO_4$ Electrode to Halide Ions

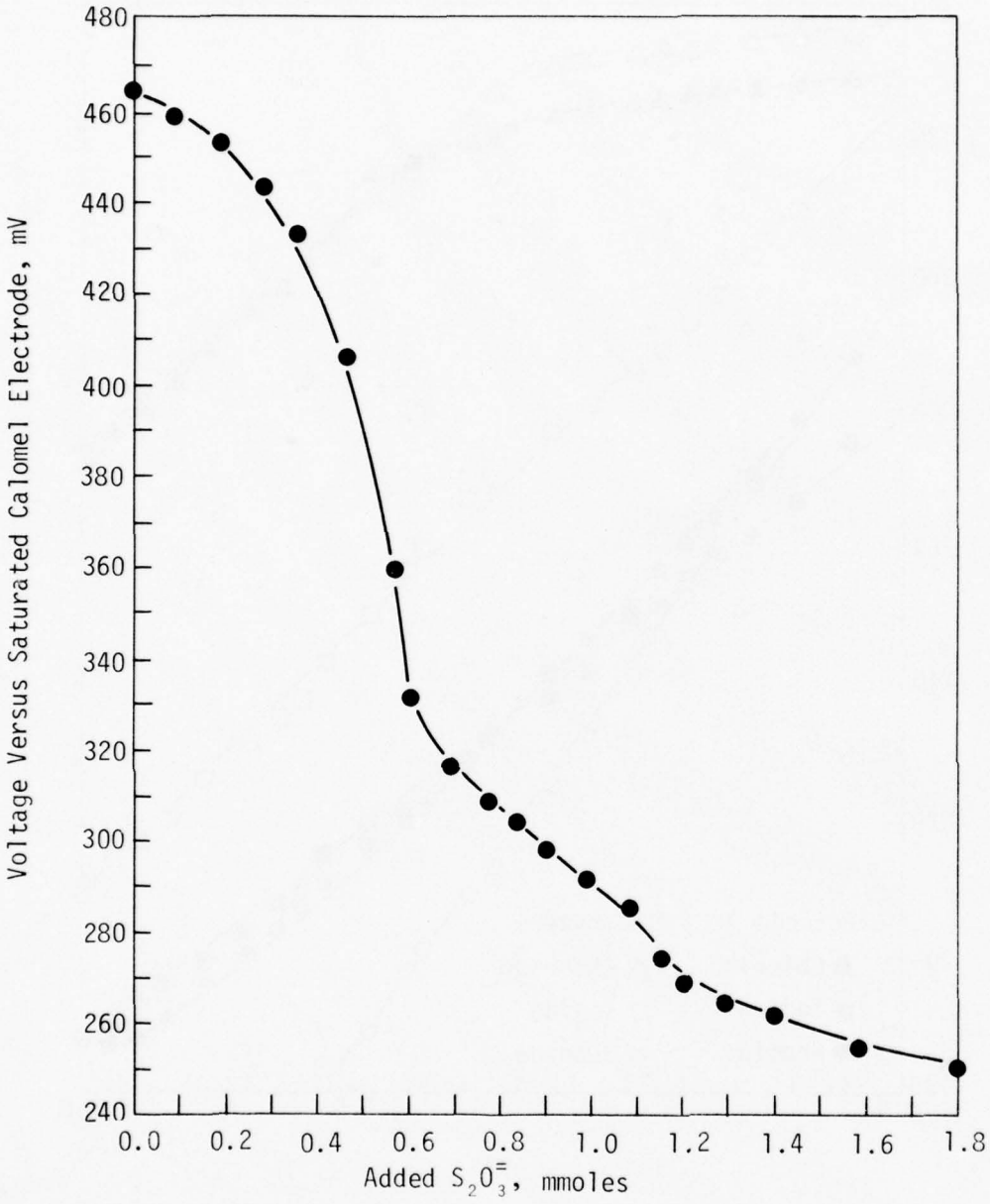


Figure 6. Response of $Ag_6I_4WO_4$ Electrode to 1.00×10^{-3}M $AgNO_3$ Solution with Added $Na_2S_2O_3$

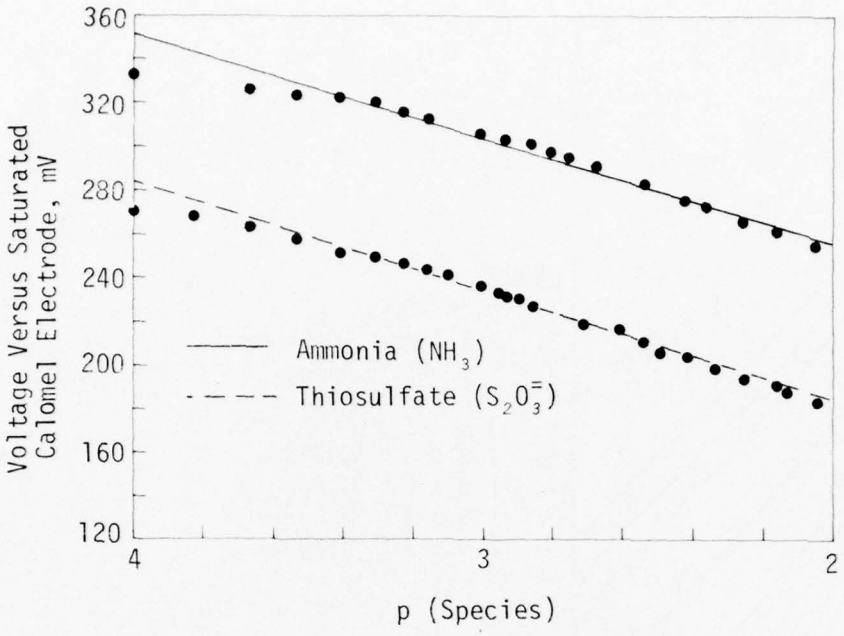


Figure 7. Response of $Ag_6I_4WO_4$ Electrode to Thiosulfate and Ammonia

probably $Ag_2S_2O_3$ and/or Ag_2S, was observed to form at the electrode surface. The effect of adding NH_3 to a silver-free 0.100M KNO_3 solution is also shown in Figure 7. No precipitate formed at the electrode surface, but the decreasing response clearly indicates that silver-ion concentration at the electrode/solution interface was lowered by the formation of silver-ammine complexes.

Voltammetric Response

The characteristics of the $Ag_6I_4WO_4$ electrode as the working electrode in a three-electrode, polarographic system were studied. The other two electrodes were the Orion Double Junction No. 90-02 Reference Electrode and a platinum-foil, counter electrode. The instrumentation consisted of a Health Polarography System, a Sargent SR Recorder, and a Sargent 1800-rpm Electrode Rotator.

Figure 8 shows a series of current/voltage curves for different silver-ion concentrations. With each addition of silver nitrate to the supporting electrolyte, the current at +0.37 V increased cathodically in a manner directly proportional to the silver-ion concentration.

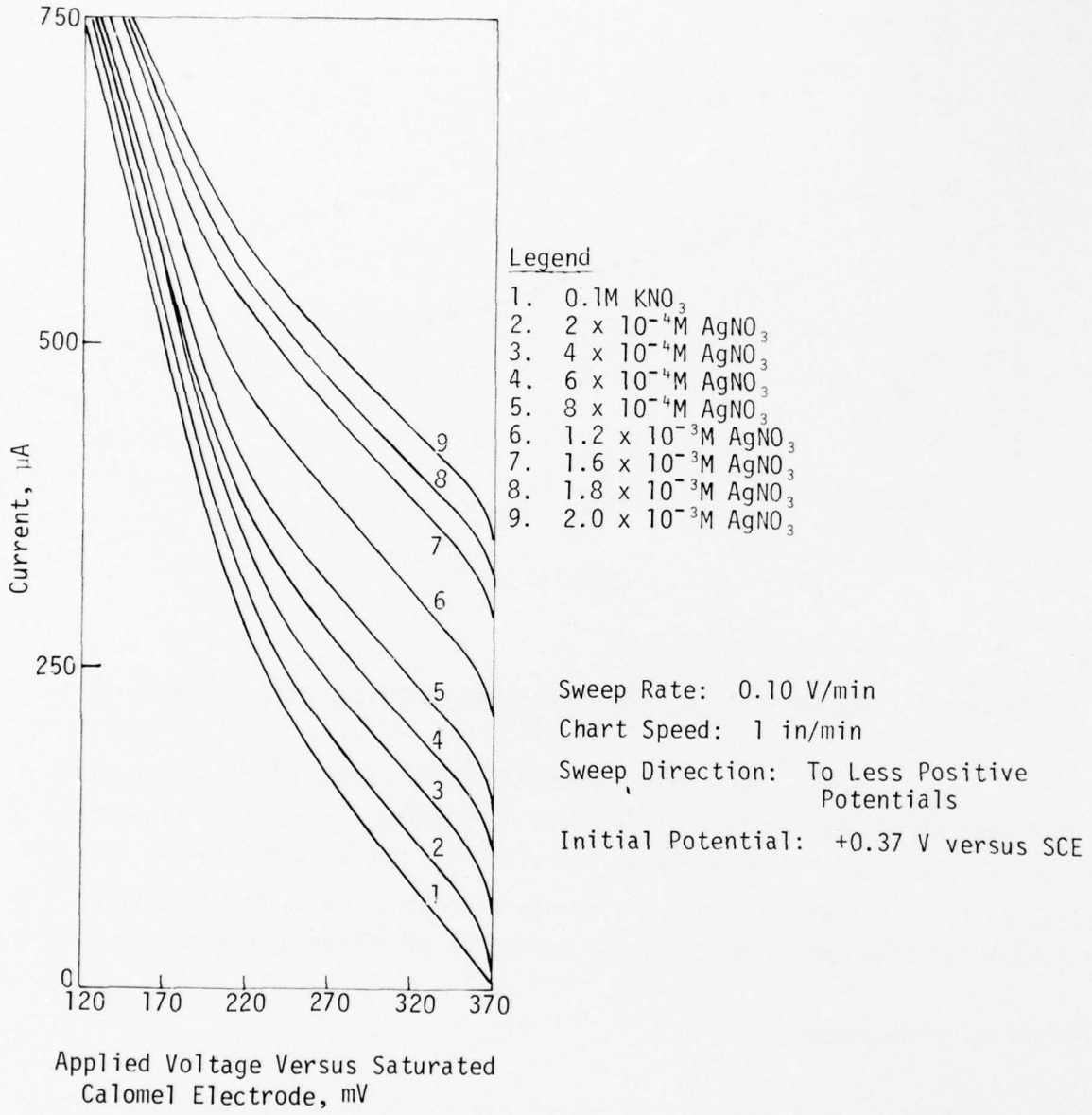


Figure 8. Current/Voltage Curves for Solutions with Different Silver-Ion Concentrations with $Ag_6I_4WO_4$ Rotated Electrode

SECTION IV

RECOVERY AND PRELIMINARY CHARACTERIZATION OF REFRACTORY ORGANICS FROM TREATED WASTEWATER

Several methods may be used for the concentration and recovery of refractory contaminants--carbon adsorption; solvent extraction; freeze concentration; ion exchange on macroreticular resins; head gas stripping with nitrogen, helium, or air; high-vacuum distillation; and reverse-osmosis solvent extraction. A brief summary of the published work in the area of recovery and quantification of trace organics is presented in Table 1. Probably the most comprehensive qualitative and quantitative analysis on sewage effluents is that reported by Marka, et al. (Ref. 49). They used vacuum evaporation to characterize rather strong Haifa secondary effluents typically possessing a COD/BOD of 30. Traditional solvent fractionation procedures were employed to yield protein, carbohydrates, anionic detergent, tannins and lignins, ether extractables, fulvic acids, humic acid, and hymathomelanic acid fractions. The humic substances were further characterized by elution from Sephadex gels to provide an estimation of the molecular weight distribution in secondary effluents. Within the ether-soluble fractions, the authors identified a series of fatty acids containing 9 to 18 carbons, found no unsaturated acids, and pointed out that the presence of fatty acids with an uneven number of carbon atoms (C_9, C_{11}, C_{15}) can be explained by conjecturing that these compounds were formed by the microbial oxidation of the unsaturated acids during the treatment processes. Alkyl benzenes and higher aromatics were also identified but not quantified.

The use of macroreticular resins to recover neutral organics present in well water contaminated by tar residues (Ref. 50) provided the source material for the identification of 14 compounds by a combination gas chromatograph/mass spectrograph. This recovery procedure should complement concentration by activated carbon, which has been shown to irreversibly adsorb polyaromatic hydrocarbons such as anthracene. Snoeyink, et al. (Ref. 51) conducted laboratory investigations to evaluate the performance of seven synthetic resins (including XAD-4 and XAD-7 non-ionic polymers) and activated carbon in the presence of p-nitrophenol and found the weak base phenol formaldehyde resin Duolite A-7 to be most promising for further study with isotherm and column testing at various pHs. A major finding was that the effluent COD from a

TABLE 1. SELECTED PROCEDURES FOR RECOVERY AND CHARACTERIZATION OF TRACE ORGANICS

Technique	Application	Remarks	References
Carbon Adsorption			
High Flow	Natural and drinking water, sewage effluent and contaminated water. Obtain solvent extract for chemical and toxicologic characterization CCE 25% of (CCE + CAE)	Inefficient, costly test.	41,42
Low Flow		Efficient but costly.	43,44
Minifilter		Reliable, less costly and more precise than preceding methods.	36,37,38,40
Solvent Extraction			
Small Scale	Concentration of contaminants prior to chemical analysis.	Universally used; selective.	45,46
Large Scale	Concentration prior to extensive chemical and toxicologic studies.	Selective, costly, and less time-consuming than carbon adsorption.	47,48
Vacuum Evaporation	Concentration of NVTOC prior to chemical characterization.	Used following centrifigation of effluent.	49
Macroreticular Resins	Same as carbon adsorption.	Effective for concentration of neutral compounds and aromatics.	50,51
Hybrid Procedures*	Natural and drinking water chemical and toxicologic studies.	Very expensive and less selective than preceding methods. Avoids harsh conditions.	52
Direct Measurement			
Head Gas Stripping			
Nitrogen	Concentration of volatile substances, dissolved and entrained gases and solutes from aqueous samples.	Use of high-resolution gas chromatography and mass spectroscopy to quant. natural and synthetic organics in 5-ℓ samples.	53
		5-mℓ sample, adsorption on Tenex & flushing to gas chromatography.	39
Helium		10-mℓ samples, adsorption onto column, heated vapor to GC-MS.	54
Detection of Products from Oxidation or Reduction of Carbon Compounds	Instruments available for soluble and particulate organic solutions. Quantity of NVTOC.	EPA National Organics Reconnaissance Survey (1975) used NVTOC as drinking water quality parameter (sensitivity reported to 0.05 mg/ℓ).	39,55

*Drinking Water: Reverse Osmosis or Ion Exchange, Lyphilization, Solvent Extraction.

bench-scale, complete-mix reactor, aeration tank operated at a cell residence time of 20 days was significantly more amenable to removal by beds of A-7 than the equivalent system employing a cell residence time of 5 days. The authors also noted that particles greater than 0.45 μm in diameter were removed 21 and 100 percent by A-7-packed column beds for cell residence times of 0.8 and 12 days, respectively.

Direct solvent extraction procedures have been employed in only limited instances for the isolation of organic contaminants for other than identification studies. Bunch, et al. (Ref. 47) described a highly sophisticated system built around a Podbienak contactor which was designed to rapidly measure the content of synthetic or processed chemicals in the event of a hazardous spill. In an earlier investigation (Ref. 48), a Scheibel multistage countercurrent extractor and different solvents to concentrate organics from river water were employed. Although laboratory studies performed with a phenolic water system demonstrated a higher recovery efficiency with increasing impeller velocity, efficient and effective recovery was not achieved under field conditions because of emulsion formation between the natural solutes and methyl isobutyl ketone. Matthews (Ref. 56) designed, constructed, and evaluated three solvent-extraction contactors and found that a two-stage, perforated-plate column achieved a recovery efficiency equal to a comparable high-speed mixer/settler unit which was later adversely affected by emulsion formation in natural waters. It should be noted that solvent chloroform and solvent benzene extracts from direct solvent contact are the basis for standards applying to the gross organic and polynuclear aromatic content in European drinking waters (Ref. 57).

Adsorption of organic substances on active carbon has been used as the Carbon Adsorption Method in the United States since 1951 (Ref. 41). Symons, et al. (Ref. 36) have proposed a simpler, more efficient and effective apparatus and procedure for quantifying the refractory organics present in natural and finished waters--The Organics-Carbon Adsorption Method. This procedure calls for passing 60 ℓ of water through a 2-in inside-diameter by 3-in-long column packed with 70 g of 14 x 40 mesh active carbon at a flow rate of 20 mℓ/min (a contact time of 3.9 min). A salient feature of this method is a regular, periodic flushing of the carbon in the direction of sample flow to prevent

consolidation of the carbon during the run and accumulation of air pockets that impede the sample flow. Since this procedure is likely to be included in the *14th Edition of Standard Methods*, its use as a concentration method for quantifying and characterizing refractory organics from secondary and tertiary wastewater treatment facilities appears to be operationally desirable. Furthermore, both activated carbon and ion-exchange resins are feasible materials for operationally lowering the quantity of biorefractory substances and harmful trace substances from wastewater treatment plants. The principles and procedures necessary for the effective operation of the removal process should provide feedback and understanding to operating personnel if similar methods are utilized to periodically monitor effluent quality. The ability of the Organics-Carbon Minifilter to concentrate typically higher levels of organic input without unacceptable breakthrough and the chemical characterization of the recovered extracts are among the foremost items to be studied.

SECTION V
EFFLUENT ANALYSIS

MINIFILTER SAMPLING RUNS

The activated-sludge, extended-aeration treatment plant selected as the sampling site is schematically illustrated in Figure 9. The average values for the sand/anthracite-filtered, activated-sludge effluent, which was the influent to the minisampler, are shown in Table 2.

TABLE 2. WASTEWATER EFFLUENT CHARACTERIZATION

pH	9.9	Carbonate Alkalinity, as $CaCO_3$	130
Suspended Solids, mg/ℓ	4	Total Nitrogen, mg N/ℓ	9.6
Turbidity, NTU	7	Ammonia Nitrogen, mg N/ℓ	1.5
Specific Conductance, μmho/cm	820	Nitrate Nitrogen, mg NO_3^-/ℓ	14.6
Dissolved Solids, ppm	521	Total Phosphorus, mg P/ℓ	11.5
Sodium, mg/ℓ	114	Ortho-Phosphate, mg P/ℓ	8.5
Potassium, mg/ℓ	16.2	Chloride, mg Cl^-/ℓ	81
Calcium, mg/ℓ	15.5	Sulfate, mg $SO_4^=$/ℓ	96
Magnesium, mg/ℓ	3.4	Fecal Coliform, Col./100 mℓ	0
Hardness, as $CaCO_3$	95		
Total Alkalinity, as $CaCO_3$	130		

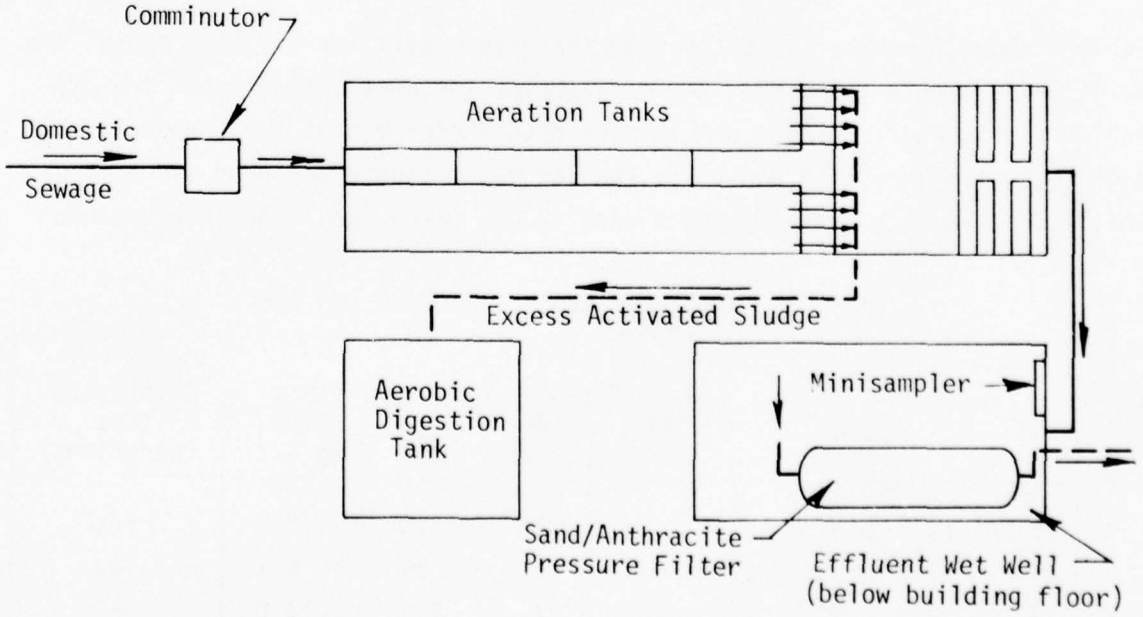


Figure 9. Activated-Sludge, Extended-Aeration Treatment Plant

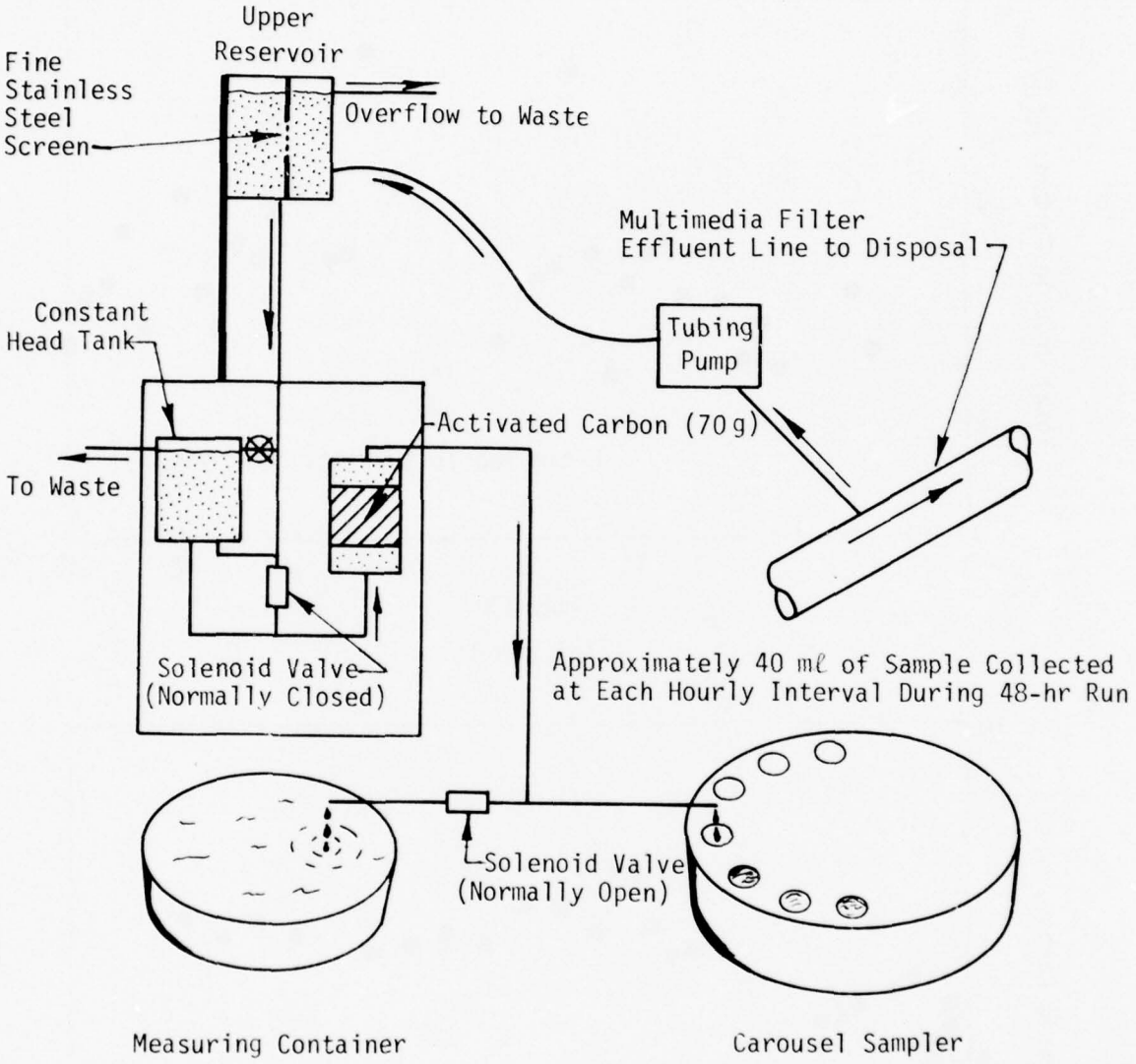
The experimental setup shown in Figure 10 was employed in the minifilter sampling runs. A carousel-type sampler collected approximately 25 mℓ of the sample in acidified Pyrex tubes at 1-hr intervals for determination of the residual nonvolatile total organic carbon (NVTOC) of the minisampler effluent. The main operational difficulty was maintaining a constant flow of the sample through the filter because of varying head pressure from the pressure filter which fed the main overhead tank. Approximately 47 ℓ of sample passed through the system during run 3 rather than the specified 60 ℓ. The location of the test equipment during runs 1 through 4 was the north wall of the filter building. This provided a suitable environment and protection from the weather. Subsequent runs were performed in the Civil Engineering Laboratories at the University of New Mexico.

Unfortunately, the activated-sludge, wastewater treatment facility experienced a rather complete and continuous process upset from January 1975 to the present. The quality of the activated-sludge effluent was extremely poor and the plant's multimedia pressure filters could only be operated for less than 1 hr before backwashing was required. Thus, the recovery procedure included passing the activated-sludge effluent through a graded-sand filter bed in the laboratory before the sampling runs were made.

Table 3 shows the data collected from the five minifilter sampling runs. The NVTOC measurements taken from the minisampler influent and effluent are presented in Figure 11. These preliminary data indicate that the comparatively high concentrations of organics in the activated-sludge effluent did not initiate a dramatic breakthrough during the sampling runs. Another apparent

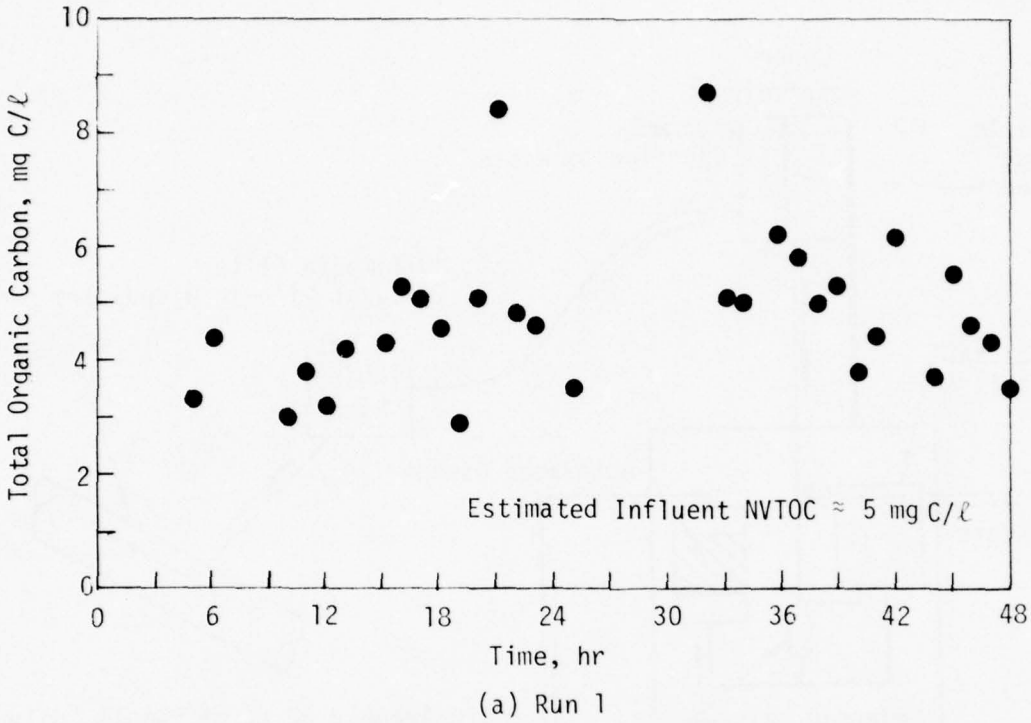
TABLE 3. DATA FROM MINIFILTER SAMPLING RUNS

Run	Date	CCE-m, mg/ℓ	Plant Effluent Characteristics				Sand/ Anthracite Filters Operational
			BOD, mg/ℓ	COD, mg/ℓ	SS, mg/ℓ	NVTOC, mg C/ℓ	
1	25 Nov 1975	1.62	-	82	22	5.0	Yes
2	11 Jan 1976	1.87	56	111	25	6.7	Yes
3	14 Jan 1976	17.05	224	276	160	24.0	No
4	27 Jan 1976	9.31	160	225	105	-	No
5	4 May 1976	1.94	-	98	31	-	Yes

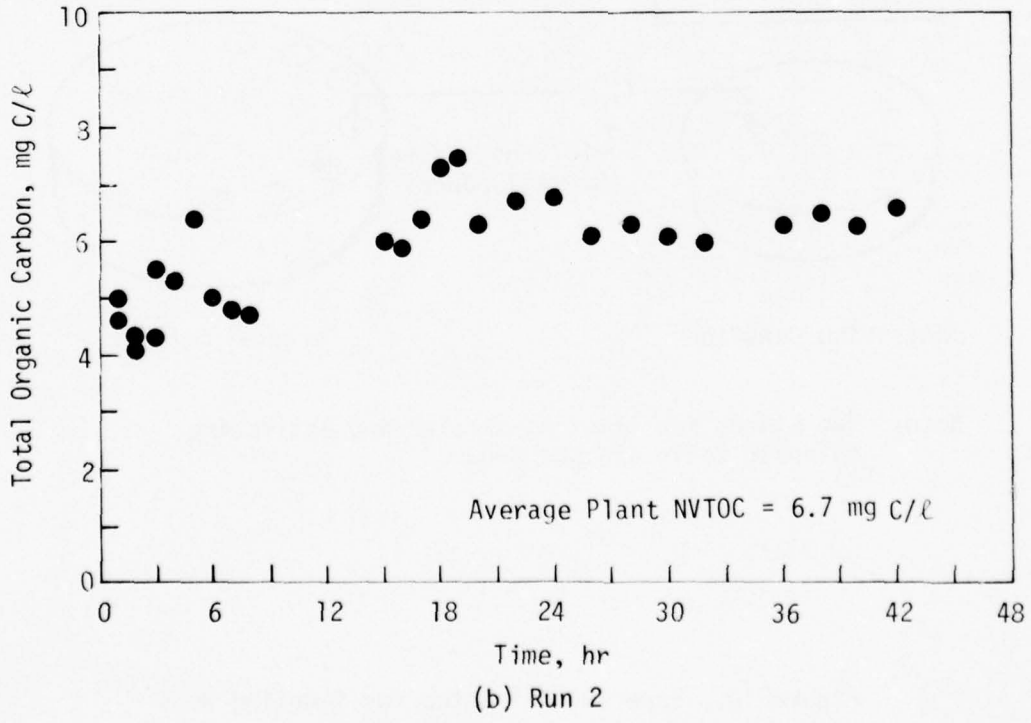


Note: Two timers for indexing sampler and activating solenoid valve are not shown.

Figure 10. Experimental Setup for Sampling Runs

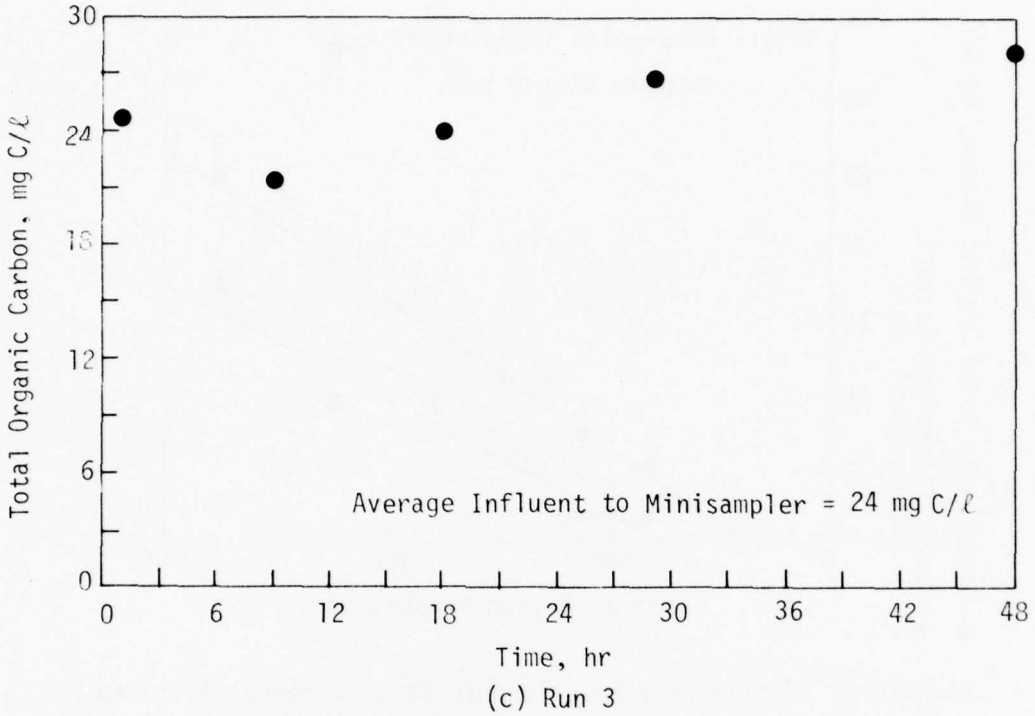


(a) Run 1

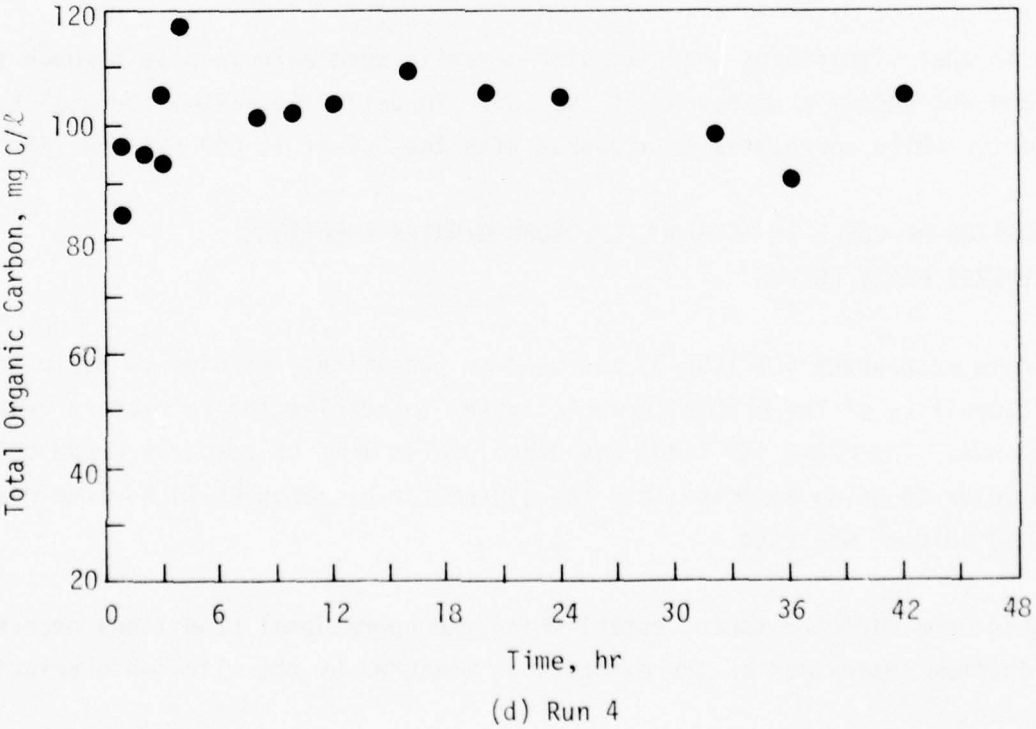


(b) Run 2

Figure 11. Nonvolatile Total Organic Carbon Data (1 of 2)



(c) Run 3



(d) Run 4

Figure 11. Nonvolatile Total Organic Carbon Data (2 of 2)

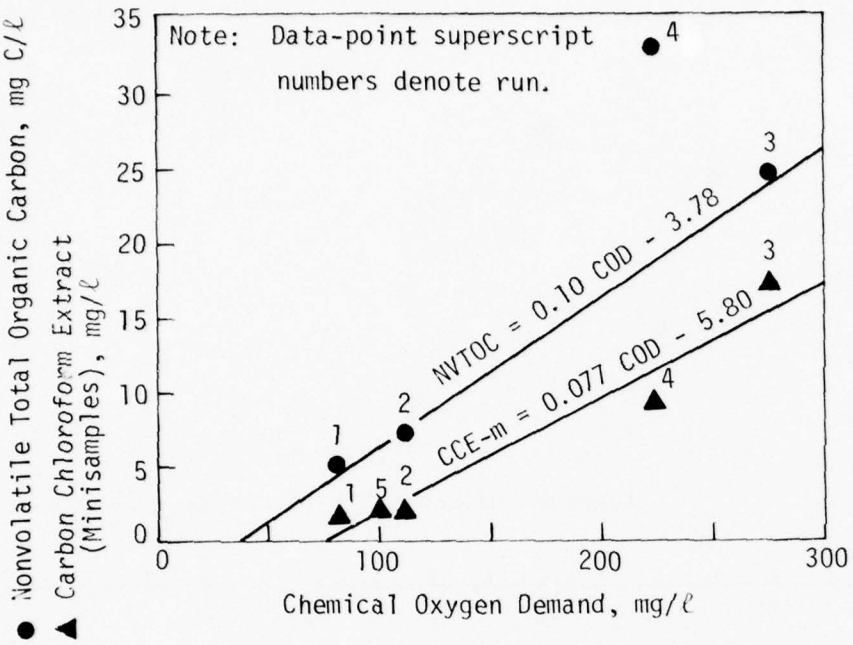


Figure 12. Preliminary Relationship Between Nonvolatile Organic Carbon, Carbon Chloroform Extract, and Chemical Oxygen Demand

fact is that significant quantities of organics were able to pass through the bed and not become a component of the CCE. To date, the wastewater quality parameter which correlates to a degree with the CCE-mf is COD (Figure 12).

SEPARATION OF CCE-3 IN METHANOL/CHLOROFORM/WATER SOLUTIONS BY REVERSE PHASE COLUMN

A single wastewater CCE (CCE-3) was used in preliminary studies to evaluate the capability of the chromatographic system to resolve the refractory organic compounds. The CCE-3 (59.7 mg) was dissolved in 1 mℓ of spectral-grade chloroform prior to being injected into the system. A Micropak CH-10 Reverse-Phase (25-cm) Column[2] was used.

Efforts were directed toward establishing the operational conditions necessary for optimum separation of the extracts as measured by the ultrasonic velocity detector.

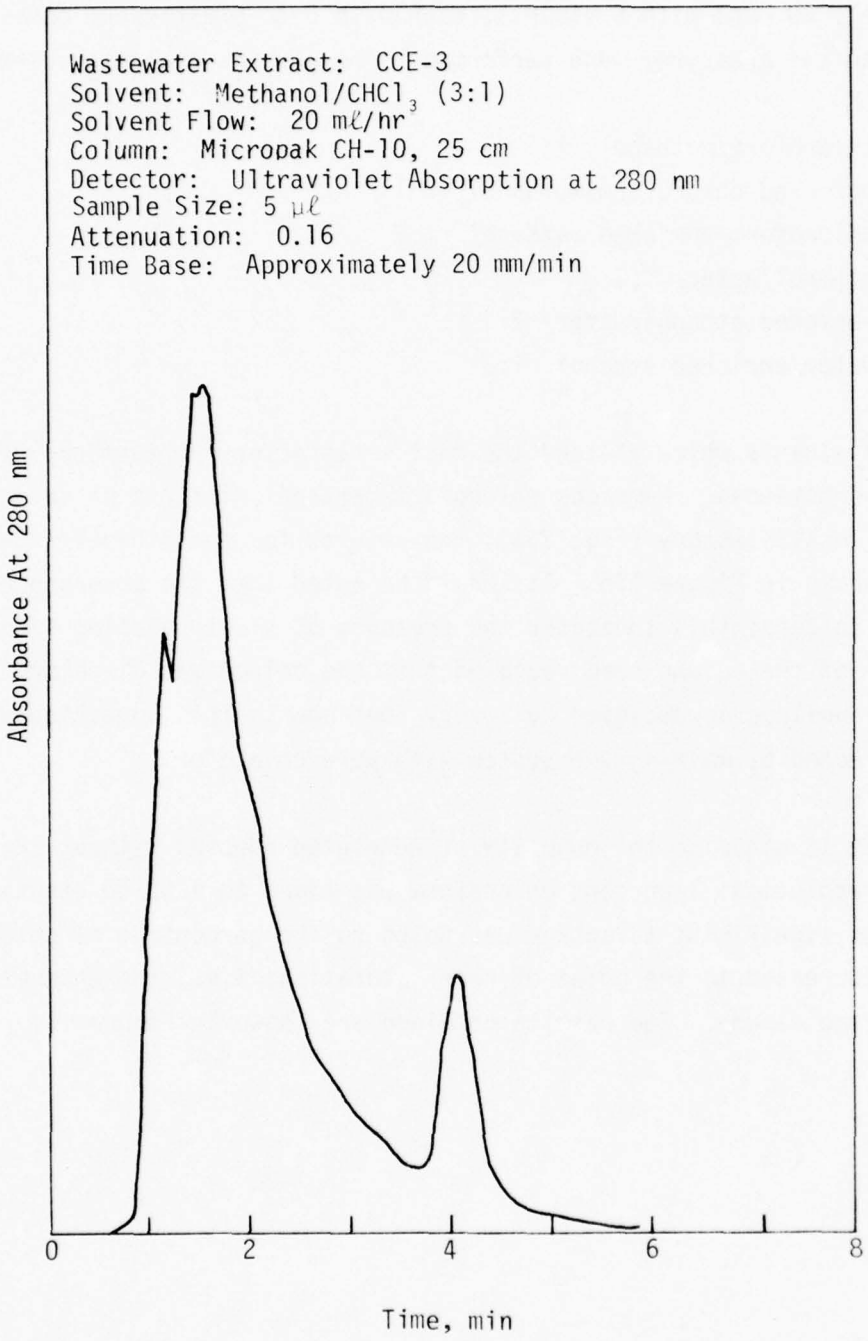
[2] Varian Associates: 611 Hansen Way, Palo Alto, California 94303.

Approximately 40 runs with 6 eluants, each with 5 to 8 different combinations of flow rate and pressure, were performed. The eluants evaluated were as follows:

chloroform/methanol 1:1
enriched chloroform/methanol 2:1
chloroform/enriched methanol 1:2
ethanol/water 1:1
enriched ethanol/water 2:1
water/enriched ethanol 1:2

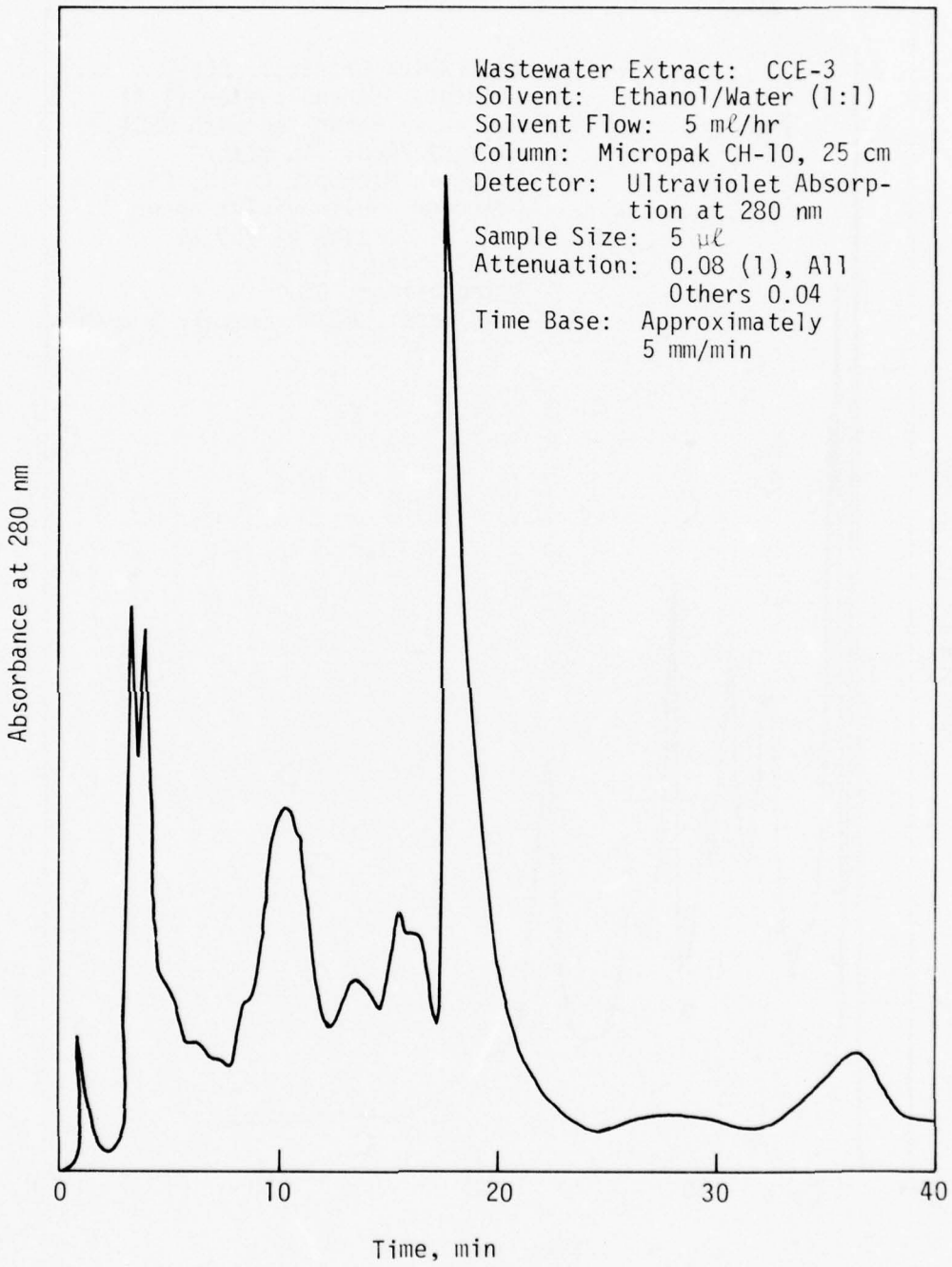
The solvent eluants which yielded the most satisfactory performance were the more polar substances. Numerous chloroform/methanol mixtures at several flow rates were unsatisfactory (Fig. 13a); the results for the ethanol/water mixtures are shown in Figure 13b. It should be noted that the absorbance does not return to zero; this indicates the presence of slowly eluting species. Disassembly of the column head revealed that the column was discolored and contained a buildup accompanied by a very foul odor. This condition was partially corrected by washing the system with pure chloroform.

In an effort to minimize the quantity of noneluted species without seriously affecting resolution, 1-percent chloroform was added to a 50:50 ethanol/water mixture. No significant advantage was noted so the percentage of chloroform added was increased to the point of near saturation; i.e., the ethanol/water mixture became cloudy. The results obtained are shown in Figure 13c.



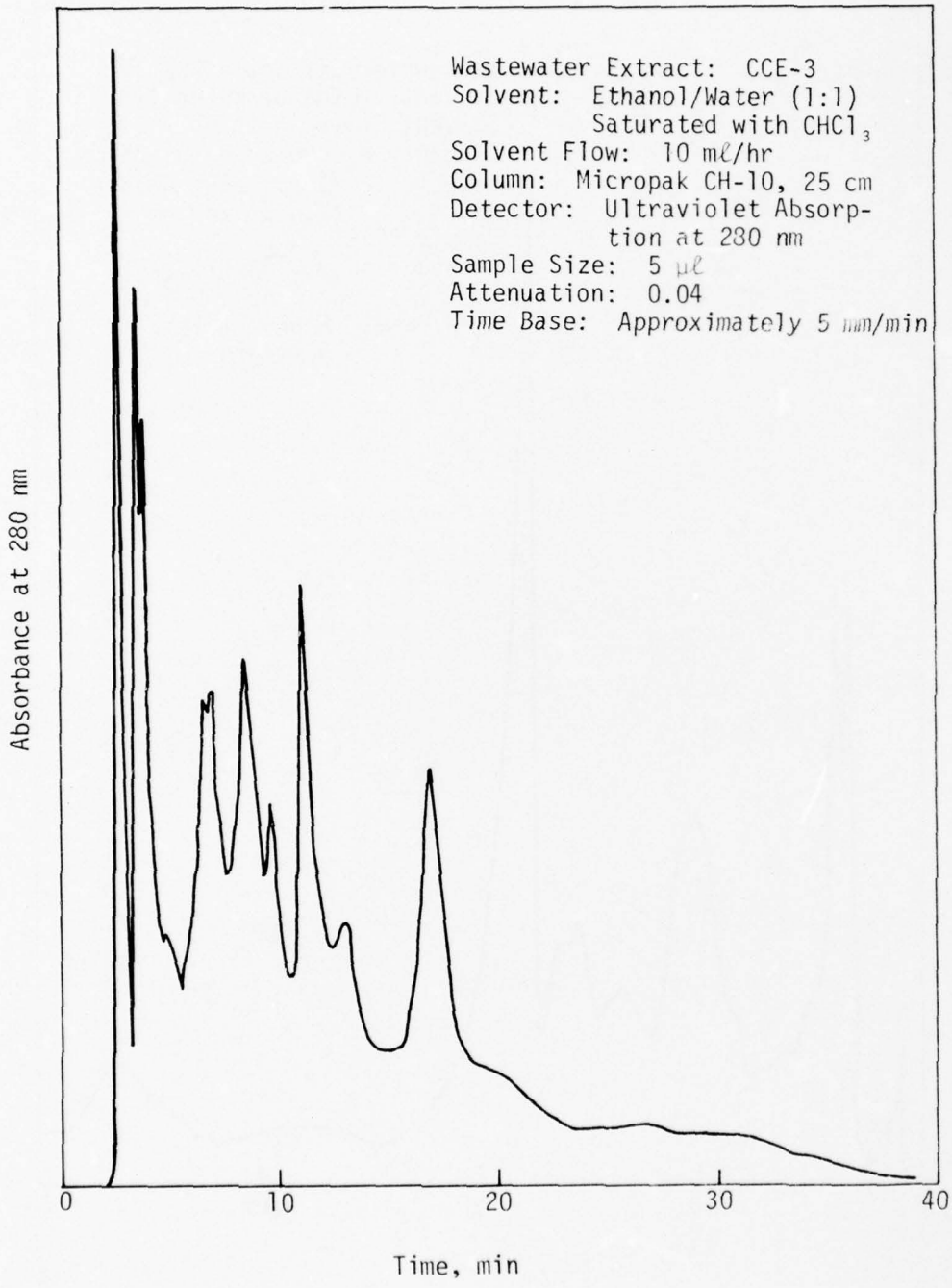
(a) Chloroform/ lethanol Mixture

Figure 13. HPLC Analysis of Wastewater Extract



(b) Ethanol/Water Mixture

Figure 13. HPLC Analysis of Wastewater Extract (continued)



(c) Ethanol/Water Mixture
Saturated with Chloroform

Figure 13. HPLC Analysis of Wastewater Extract (concluded)

SECTION VI
CONCLUSIONS AND RECOMMENDATIONS

BETA-INDUCED LUMINESCENCE DETECTOR

If a second high-pressure pump were used, a steady and reproducible flow of scintillator could be obtained and eluted solutes and scintillator could be uniformly mixed before they entered the detector. This would eliminate the erratic output. It is recommended that when the proper equipment becomes available, this be investigated.

VARIABLE-PATH-LENGTH, BETA-INDUCED LUMINESCENCE DETECTOR

The lens and its housing should be redesigned if similar detectors are to be built in the future. These detectors could probably be simplified and made less prone to leaking. Testing, calibration, and utilization of this detector will continue since its use as an HPLC detector will be the subject of a portion of William H. Rahe's Ph.D. dissertation.

ULTRASONIC VELOCITY DETECTOR

Inasmuch as the ultrasonic velocity detector has just recently become operable in its final form, there has not been time to complete calibration studies, tabulate response factors for a variety of solutes, or actually attach the detector cell to the HPLC system. Nevertheless, work is continuing in these areas since the detector system and its application will constitute the major portion of Mr. Chuan Chen's Ph.D. dissertation.

SOLID-STATE DETECTOR FOR SILVER IONS

At this point there is no clear evidence that silver metal is not plating out on the external surface of the solid-state pellet during voltammetric operation. Transport and coulometric studies will have to be made to determine if

silver ions are being conducted through the solid-state pellet to the internal mercury contact. If silver metal is plating out on the external surface, there is no advantage in using the solid-state pellet over a typical inert metal or carbon electrode when detecting silver ions voltammetrically.

The $Ag_6I_4WO_4$ electrode can be used as a silver-ion potentiometric detector in HPLC if interfering substances are not present. It will also function as a potentiometric detector for anions forming insoluble silver salts and species forming stable silver complexes, provided the solubility products of the insoluble salts are exceeded and the conditional formation constants of the silver complexes are sufficiently large to form stable complexes at the electrode/solution interface. Its use as a voltammetric detector is not established at this point; further work must be done to determine its capabilities in that area.

EFFLUENT ANALYSIS

Recommendations with respect to the effluent analysis are that a multipump capability would be desirable to more effectively separate the substances and that other columns, solvents, and CCE materials should be investigated. The Chemistry Department of the University of New Mexico has offered the use of their gel permeation chromatography unit for separation of the extracts. This unit is now equipped with a refractive-index and an ultraviolet-absorption detector.

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APPENDIX A
ULTRASONIC VELOCITY DETECTOR UNIT

This appendix functions as a user's manual for the ultrasonic velocity detector unit in that it contains descriptions, including circuit diagrams of the various modules, and operating, calibrating, and troubleshooting procedures. The circuit diagrams are current; recent modifications to the system are discussed in Section III.

FUNCTIONAL CONTROLS

Front Panel

ON-OFF Switch. The ON-OFF switch turns the power on or off; a pilot lamp indicates operation. A 4-amp fuse in the primary circuit is located on the rear of the chassis.

RECEIVER Connector. This BNC connector connects the receiver module input signal to the receiving transducer in the detector cell.

TRANSMITTER A and TRANSMITTER B Connectors. These BNC connectors connect the output signal of the two transmitter modules to the two transmitting transducers in the detector cell.

COMP-LOCAL Switch. This DPDT, on-none-on, toggle switch (SW2) selects either external computer control or internal control through the logic circuit.

TRANSMITTER A and TRANSMITTER B Switches. These SPDT, on-none-one, toggle switches (SW3, SW4) turn the detector cell transmitting transducers on or off. When transducer A is on, sample-and-hold A (S&HA) is in the *sample* mode for calibration of S&HA (transmitter B in off position). These switches are bypassed when the detector is operated in the automatic mode.

MAN-AUTO Switch. This 4PDT, on-none-on, toggle switch (SW1) provides the option of operating the detector unit manually or automatically. When operated manually, the logic circuit is nonfunctional and the digital panel meter (DPM) is triggered internally. When operated automatically, the DPM is triggered by a down-going pulse (DPM TRIG) and the readout is held until the next pulse triggers it again. Also, S&HB is held in the sample mode when this switch is in the MAN position.

FUNCTION Switch. This 4-pole, 10-position switch (SWA) permits selection of readouts on the DPM and outputs to the recorder. The DPM reads the phase shift in terms of -1/10 of 1 mV directly from the output of the phase meter when this switch is at B. When the switch is at A, the positive value of the phase shift is shown on the DPM. In position SIG the DPM reads the output of OA1, the difference in phase shift between the two transmitting transducers when operated automatically. Positions +40 V, +15 V, -15 V, and +5 V provide the power supply voltage checks. Positions X1, X10, and X100 provide three attenuations for the DPM so as to permit any voltage to be checked when necessary. The recorder only responds to the signals when this switch is at SIG or A.

PERIOD TIME Switches. COARSE A and COARSE B are 1-pole, 10-position switches (SW5, SW6) and FINE A and FINE B are 10-turn potentiometers (R18, R19). The switches alternately control the on-time of the transmitting transducers and therefore control the cycle time of the unit (in 0.1-sec steps). They are only effective when the unit is operated automatically.

OUTPUT (BNC Connectors). SIG connects the output signal from the receiver module to one channel of the frequency converter. REF connects the output from the 1-MHz oscillator to the second channel of the frequency converter. LOC OSC connects the output of the local oscillator to the frequency converter. RECORD connects the inverted phase shift to a strip chart recorder.

Top Chassis

OTR Unit

This unit includes the 1-MHz oscillator, the local oscillator, two transmitter modules, and the receiver module.

GATE A and GATE B Connectors. These miniature RF connectors connect via shielded cables the A and B gate signals originating in the logic circuit to two transmitters.

REF Connector. This miniature RF connector connects the 1-MHz reference signal to the front panel REF output connector via a shielded cable.

XMTR A and XMTR B Connectors. These BNC connectors connect the output of the transmitters to the front panel TRANSMITTER A and TRANSMITTER B connectors via shielded cables.

REC IN Connector. This BNC connector connects the reciver module input to the front panel RECEIVER connector via a shielded cable.

REC OUT Connector. This BNC connector connects the output of the receiver module to the front panel SIG connector via a shielded cable.

LOC OSC Connector. This BNC connector connects the output signal of the local oscillator to the front panel via a shielded cable.

DC IN Connector. This 6-contact, miniature connector brings in +40 V, +15 V, -15 V, +12 V (for crystal oven), +5 V, and common from the power supply.

2nπ Controls

2nπ Switch. The first five positions of this 1-pole, 10-position switch (0-4) provide positive voltages from 0 to +14.4 V in 3.6-V steps to point 2nπ. Position 5 is open for calibration purposes and the remaining positions (6-9) are grounded.

TP. This black tip jack provides a test point for 2nπ during calibration.

n. These four 20-kΩ trimming potentiometers are used to calibrate the exact voltages of 2nπ (3.6, 7.2, 11.8, and 14.4 V).

V TEST

These green tip jacks are marked 1, 10, and 100. They are connected to X1, X10, and X100 points of SWA, respectively.

Logic Unit

DIV OUT. This 20-kΩ trimming potentiometer serves as an output offset potentiometer from divider AD-427J (DIV).

DIV X. This 20-kΩ trimming potentiometer serves as an external trimming device for the X input (denominator) of the divider.

OA4(T) and OA1(T). These 50-kΩ trimming potentiometers serve as offset potentiometers for the operational amplifiers AD-118.

S&HA(T) and S&HB(T). These 10-kΩ trimming potentiometers provide the offset for the sample-and-hold modules DATEL SHM-4.

OA2(T) and OA3(T). These 20-kΩ trimming potentiometers provide offset for the operational amplifiers AD-101.

Rear Chassis

PHASE IN Connector. This BNC connector connects the phase meter output signal to the detector unit via a shielded cable.

OPERATING INSTRUCTIONS

Setup

NOTE

Before operating this equipment, familiarize yourself with the operation of the ADYU-524A4 phase meter and the ADYU-306 frequency converter by referring to the manufacturer's instruction manuals (ADYU Electronics, Inc.; 2517 E. Norwich St., Milwaukee, Wisconsin 53207).

(1) Connect transmitting and receiving transducers of the detector cell to the detector unit via proper connectors.
(2) Connect E1 IN, E2 IN, and LO IN of the frequency converter (ADYU-306) to the SIG, REF, and LOC OSC output connectors of the detector unit, respectively.
(3) Connect E1 IN and E2 IN of the phase meter to E1 OUT and E2 OUT of the frequency converter, respectively.
(4) Connect the DVM OUTPUT of the phase meter to the PHASE IN connector on the rear chassis of the detector unit.
(5) Plug the line cord into 115 V, 50/60 Hz. Turn on the detector unit and allow 5 min for warmup.

Manual Operation

Steady Phase Measurement. If the velocity of the ultrasound wave is to be measured in a solution of known composition, the following procedure is followed:

(1) Set COMP-LOCAL switch to LOCAL position.
(2) Set AUTO-MAN switch to MAN position.

(3) Calibrate the 0° SET and 360° SET of the phase meter according to the phase meter instruction manual. While the FUNCTION switch of the detector unit is at B, the DPM will indicate a voltage of either 00000 or -36000 in units of 1/10 of 1 mV.

(4) Turn FUNCTION switch to A. The DPM should now display a positive voltage of the same absolute value as that at B. (Refer to calibration procedure if this does not occur.)

(5) Turn on TRANSMITTER A. The voltage displayed on the DPM will be the phase shift between the transmitting transducer A and the receiving transducer in 1/100 of 1 deg.

(6) Turn TRANSMITTER A off and turn TRANSMITTER B on. The DPM now reads the phase shift between transmitting transducer B and the receiving transducer.

NOTE

The difference in readings obtained in steps (5) and (6) will be the phase shift difference between the two transmitting transducers.

(7) Calculate the velocity of the ultrasound wave using the above data. (See, for example, reference 35.)

Flow System Measurement (Sample Flowing Through Cell). In this stage only, transmitting transducers A or B may be used in one measurement as follows:

(1) Make all calibrations as above.

(2) Set FUNCTION switch to A position.

(3) Connect a strip chart recorder to the RECORD output of the detector unit via the offset device.

(4) Turn either TRANSMITTER A or TRANSMITTER B on.

(5) Set the $2n\pi$ switch to the proper position. (See $2n\pi$ selection.)

(6) Balance the recorder by adjusting the potentiometer of the voltage offset device.

(7) Inject a sample into the separation column. The recorder output will now indicate the velocity change, which can be interpreted as the change in concentration, versus time.

Automatic Operation

(1) Make all necessary calibrations as above.
(2) Set COMP-LOCAL switch to LOCAL position.
(3) Set MAN-AUTO switch to AUTO.
(4) Adjust the PERIOD TIME switches of both A and B according to Table A-1 to provide the desired width of the generated pulses which will turn on the transmitting transducers A and B. (Pulse A must be 0.1 sec longer than pulse B.)
(5) Set $2n\pi$ switch to the proper position. (See $2n\pi$ selection.)
(6) Connect and balance the recorder as for manual operation.
(7) Inject a sample and observe the recorder output.

NOTE

If no pulse is generated in step (2) (i.e., the DPM does not trigger), a starting pulse may be generated by first setting the COMP-LOCAL switch to COMP and then back to LOCAL. Once the pulses are generated they will continue.

CALIBRATION PROCEDURES

The detector unit should be calibrated on a monthly basis or whenever poor performance is detected. The following procedures are used:

(1) Set switches on the front panel to LOCAL and MAN positions.
(2) Calibrate X10 and X100 of SWA as follows:
    (a) Apply a standard voltage of approximately 4 V between tip jacks 1 and G of V TEST (top chassis); set FUNCTION switch to X1; and record the voltage displayed on the DPM.
    (b) Apply the above standard voltage between tip jacks 10 and G; change FUNCTION to X10; and again record the reading on the DPM.

NOTE

If the second reading is not 1/10 of the first reading, the 2-kΩ trimming potentiometer of SWA must be adjusted.

    (c) Apply the same standard voltage between G and 100; set FUNCTION at X100; and again record the voltage displayed on the DPM. (This value should be 1/100 of the first one.)

(d) Adjust the 1-kΩ trimming potentiometer of SWA to obtain the correct value.

(3) Calibrate 2nπ OUT as follows:

(a) Connect TP of 2nπ control to tip jack 10 of V TEST.

(b) Set FUNCTION switch to X10.

(c) Set 2nπ switch to position 4.

(d) Adjust n = 4 trimming potentiometer to provide display of exactly 14400 on DPM.

(e) Set 2nπ switch to position 3.

(f) Adjust n = 3 trimming potentiometer to provide display of exactly 11800 on DPM.

(g) Set 2nπ switch to position 2.

(h) Adjust n = 2 trimming potentiometer to provide display of exactly 07200 on DPM.

(i) Set 2nπ switch to position 1.

(j) Connect TP to jack 1 of V TEST.

(k) Set FUNCTION switch to X1.

(l) Adjust n = 1 trimming potentiometer to provide display of exactly 36000 on DPM.

(4) Calibrate divider as follows:

(a) Remove S&HB and S&HA from socket.

(b) Set 2nπ switch to position 5 (open).

(c) Apply proper standard voltage to TP of 2nπ switch and the output of S&HB according to Table A-2.

(d) Adjust trimming potentiometers DIV OUT and DIV X according to Table A-2.

(5) Calibrate OA3, OA4, and related components as follows:

(a) With S&HA and S&HB still excluded from the circuit and 2nπ switch at position 5, ground TP of 2nπ switch and ground the output of S&HB.

(b) Adjust trimming potentiometers OA3(T) and OA4(T) to obtain a zero-volt output from both OA3 and OA4.

(c) Using a voltage source of about +3.5 V, measure the value accurately with the DPM by connecting to V TEST and tip jacks 1 and G. Then, apply this voltage to TP with the output of S&HB still grounded. Adjust RK to obtain the negative value of

TABLE A-1. PERIOD TIME SWITCH POSITIONS

Coarse Position	Fine Position	Pulse Width, (sec)
1	79.7	0.1
2	64.7	0.2
3	51.4	0.3
4	38.9	0.4
5	23.8	0.5
6	10.1	0.6
7	0	0.7
8	0	0.8
9	0	0.9
0	0	1.0

Note: Applicable to both A and B.

TABLE A-2. DIVIDER BALANCES FOR X AND OUT

Step	Trim Adjustment	X-Input, V	Z-Input, V	E_{out}
1	DIV OUT	-1	0	Adjust for Zero
2	DIV X	-1	+1	Adjust to -10.00 V[a]
3	DIV X	-1	-1	Record E_{out}
4	DIV X	-1	-1	Adjust to +10 V + e[b]

[a] Voltage can be displayed by using X10 of the FUNCTION switch.

[b] e = 1/2 difference between E_{out} of step 3 (+10 V + 2e) and +10 V.

this previously determined voltage at the output of OA4.

(d) Ground TP and apply the above voltage (≃ 3.5 V) to output of S&HB. An exact negative output can be obtained from OA4 by adjusting RL.

(6) Calibrate OA1, OA2, and related components as follows:

(a) Remove S&HA from its socket.

(b) Apply zero volt from the phase meter to the detector unit. (See phase meter manual.)

(c) Connect input and output of S&HA together with a shorting lead.

(d) Adjust trimming potentiometer OA1(T) and OA2(T) to get zero-volt output from OA1 and OA2. This may easily be checked by setting FUNCTION switch to A and then to SIG.

(e) Ground input of RA and apply -3.6 V from the phase meter to OA2. (See manual.)

NOTE

RA', RB', RC', RD', and RE' are large-value resistors (10 to 50 MΩ) which are placed in parallel with RA, RB, etc. to achieve exact unity gain of the operational amplifiers.

(f) With FUNCTION set at A, change resistor RD' or RE' to obtain exactly 3.6 V.

(g) Change FUNCTION switch to position SIG. DPM should now indicate -3.6 V. Change resistor RB' or RC' to obtain exactly -3.6 V.

(h) Reconnect input and output of S&HA. DPM should now display zero volt. This can be achieved by changing resistor RA' or RC'. If RC' was changed, step (g) must be checked again.

(7) Calibrate S&HB as follows:

(a) Plug S&HB back into the socket.

(b) Ground input of the S&HB and adjust S&HB(T) to obtain zero-volt output.

(c) Set MAN-AUTO switch to AUTO position and adjust PERIOD A and B to a moderate time interval (0.2 to 2.0 sec).

(d) With the input grounded, connect the output of S&HB to an oscilloscope set at a range of 1 mV and trace the signal with the oscilloscope set for AC measurement. Use the hold offset

adjustment to obtain as flat a horizontal trace as possible. If there is difficulty obtaining a flat response (with the exception of small spikes), the PERIOD setting is too low. A longer time interval should be selected, and this step should be repeated.

(e) Apply +3.6 V to the input of S&HB and adjust the hold offset again.

(f) Repeat steps (d) and (e) several times until the best results are obtained for both tests.

(8) Calibrate S&HA as follows:

(a) Ground the input of S&HA and adjust S&HA(T) to read zero-volt output with MAN-AUTO switch set to MAN.

(b) Adjust the hold offset as for S&HB [steps (7c) through (7f)].

dc POTENTIAL CHECK

Since the +40 V, +15 V, -15 V, and +5 V dc power supplies are also connected to the FUNCTION switch, the dc potential can be checked any time by setting FUNCTION to the desired position. Defective power supplies can then be detected by observing the readings on the DPM.

REPLACEMENT OF ELECTRONIC COMPONENTS

All components, except those which are in the circuits of the two transmitter modules and the resistors which are connected to the operational amplifiers OA1 and OA2, may be replaced freely when defective. Components in transmitter modules A and B are matched (4 percent) pairs for the two modules to provide identical operating conditions for the two transmitters. The 10-kΩ resistors connected to OA1 and OA2 are matched to better than 0.01 percent to provide unity gain. The exact match is achieved by connecting large-value resistors in parallel with the 10-kΩ resistors.

TROUBLESHOOTING

Little trouble should be experienced with this detector unit, other than defective parts. These may easily be detected by careful calibration. The following problems may occur at more frequent intervals:

(1) During any measurement, the phase shift displayed on the DPM should be stable to better than ± 0.05 mV and the output of the recorder should not show noise of more than 1 mV. When the performance of the detector unit is poorer than specified, the phase meter should be carefully balanced again. (See the operation manual for the ADYU524A4.)

(2) If spikes are shown on the recorder output, the S&H offsets must be adjusted.

(3) The $2n\pi$ output should be checked when nonlinearity of the recorder output is detected. Linearity is best checked by filling the cell with solutions of different concentrations; a plot of output versus concentration should be linear.

(4) When it is impossible to balance the recorder output by the voltage offset device, the voltage offset battery needs to be replaced.

$2n\pi$ SELECTION

The parameter n is the number of full waves (2π) delayed between the transmitter and the receiver other than the portion of phase shift delay obtained from the phase meter. The number of full waves shifted depends on two variables--the distance between the receiver and the transmitter and the velocity of sound in the medium between the receiver and the transmitter. Therefore, n depends on the particular detector cell being used and the solvent passing through the cell. For the particular cell used in this development effort, the value of n was 3. The parameter n may also be calculated from the known sound velocity in a calibrating medium (such as distilled water) and the approximate distance between the transmitter and the receiver in a particular cell by the equation

$$n = \frac{fr}{V} - \frac{\Delta\theta}{2\pi} \qquad (n = 1,2,3, \ldots)$$

where f = frequency of the sound (1 MHz in the detection system described here), r = approximate distance between transmitter and receiver, V = velocity of sound in the calibrating medium, $\Delta\theta$ = phase shift measured by the phase meter, and 2π = 360 deg. The calculated value of n should, of course, be rounded off to the nearest integer.

APPENDIX B

CIRCUIT DIAGRAMS

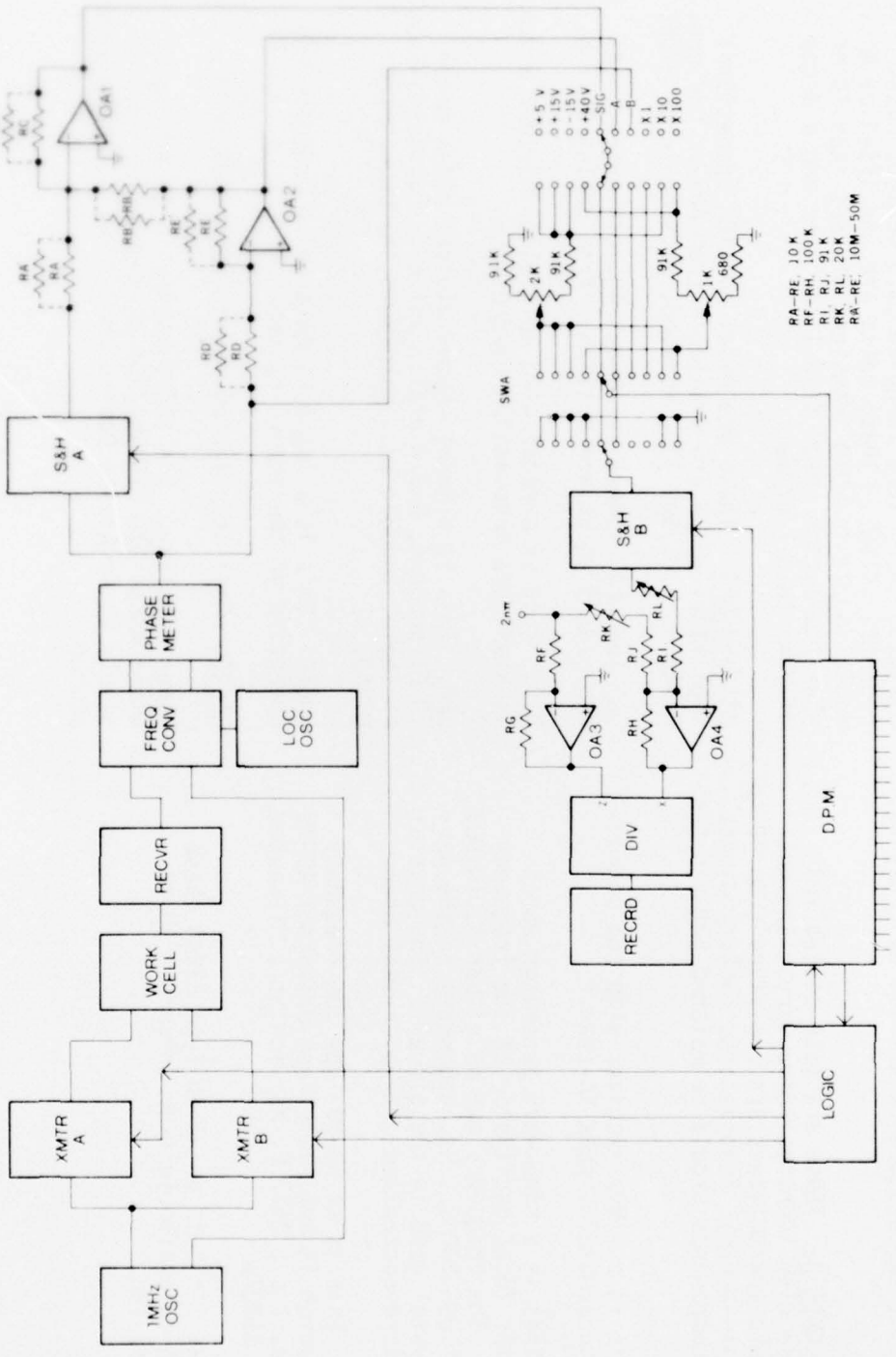

Figure B-1. Ultrasonic Velocity Detector Unit

CRITICAL COMPONENTS

1-MHz OCS. This sine-wave oscillator should have a frequency of 1,000,000 ± 1 Hz. The crystal in the circuit is temperature-controlled by a crystal oven.

XMTR A and XMTR B. These are gate-controlled transmitters with identical circuitry. The outputs of these transmitters are amplified from 40 to 80 V (peak-to-peak). Transistors, chokes, diodes, and other components should be matched between the two units.

RECVR. This is a 1-MHz receiver with the output amplified to about 3 V peak-to-peak.

LOC OSC. This is a sine-wave generator which serves as the local oscillator of the frequency converter. The frequency may be either 1,010,000 ± 1 Hz or 1,005,700 ± 1 Hz, depending on the particular crystal used in the circuit. The crystal is temperature-controlled with a crystal oven.

FREQ CONV. This is an AD-YU Type 306 frequency converter which is available from Universal AD-YU Electronics, Inc., 2517 E. Norwich St., Milwaukee, Wisconsin 53207.

PHASE METER. This is an AD-YU Type 524A4 phase meter which is available from Universal AD-YU Electronics, Inc.

S&HA and S&HB. These are sample-and-hold units (Model SHM-4) which are available from Datel Systems, Inc., 1020 Turnpike St., Canton, Massachusetts 02021. These units are specified as having a sample-to-hold transient of less than 10 mV when the switch speed is 0.1 to 1 sec and a droop of less than 1 mV/sec.

OA1 and OA4. These are Model AD-118A operational amplifiers which are available from Analog Devices, Route 1, P.O. Box 280, Norwood, Massachusetts 02062.

OA2 and OA4. These are Model AD-101A operational amplifiers which are available from Analog Devices.

DIV. This is a Model 427J multiplier/divider which is available from Analog Devices.

DPM. This is a Model AN2544 digital panel meter (0.01 percent, 4-3/4 digit) which is available from Analogic, Audubon Rd., Wakefield, Massachusetts 01880.

LOGIC. This is a logic circuit which controls the operation of the entire system.

RECRD. This is a Varian Model A-25 recorder.

Power Supplies. The ±15-V supply is an Analog Devices Model 920 ±15-Vdc/200-mA source and the +5-V supply is an Analog Devices Model 903 +5-Vdc/500-mA source.

Figure B-1. Ultrasonic Velocity Detector Unit (Concluded)

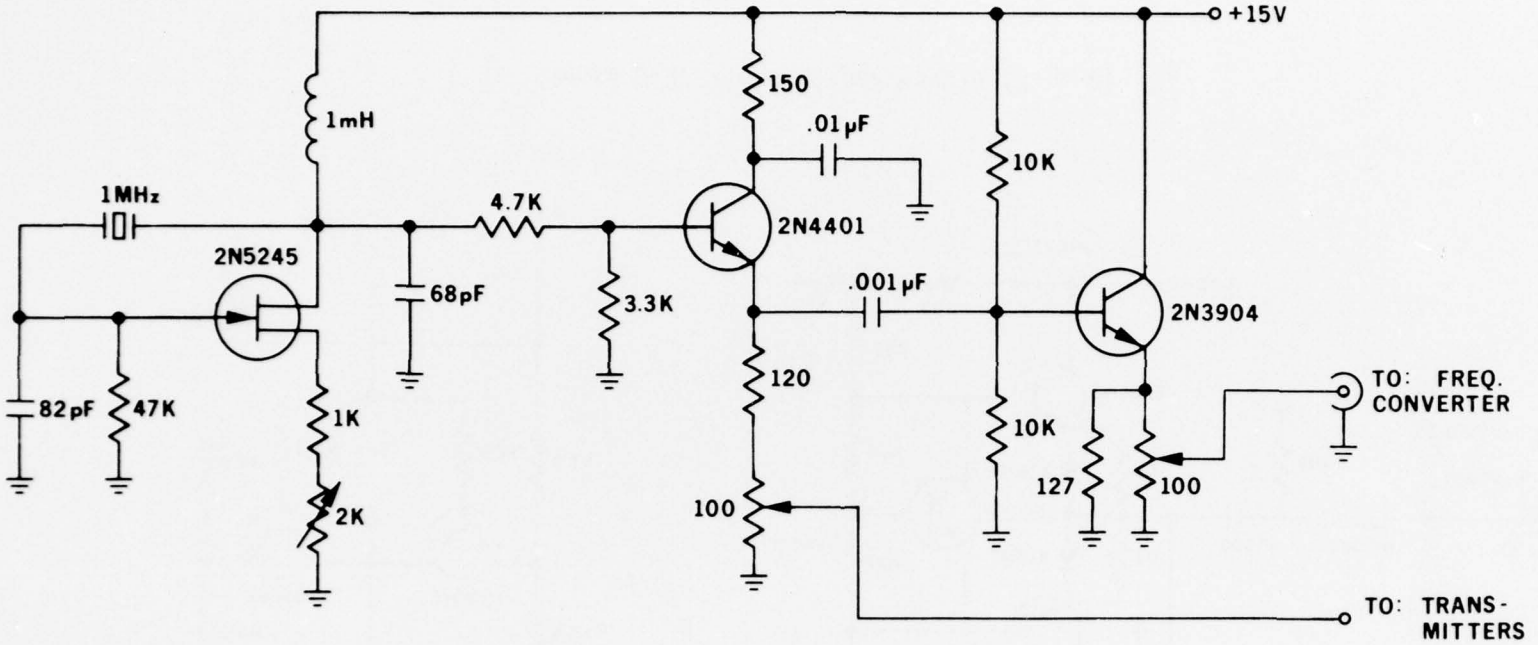

Figure B-2. 1-MHz Oscillator

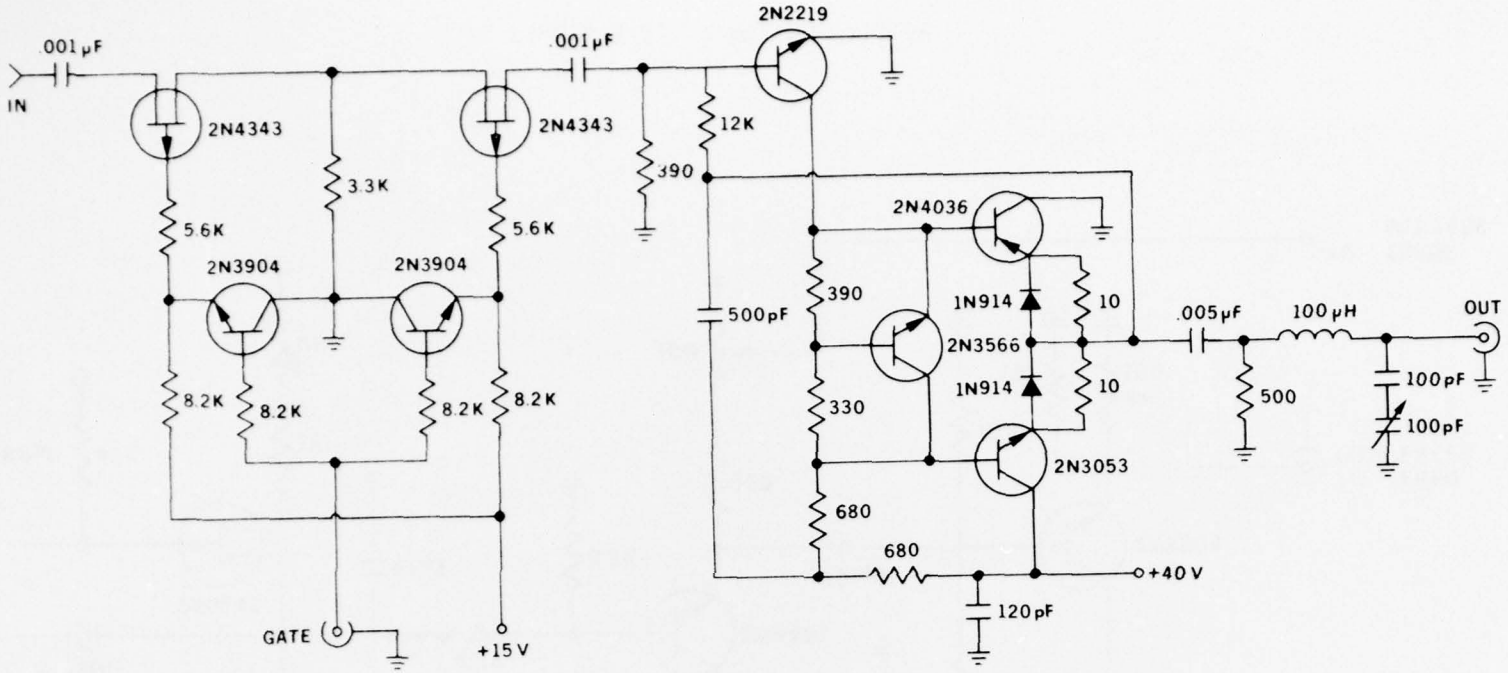

Figure B-3. Transmitter Module (A or B)

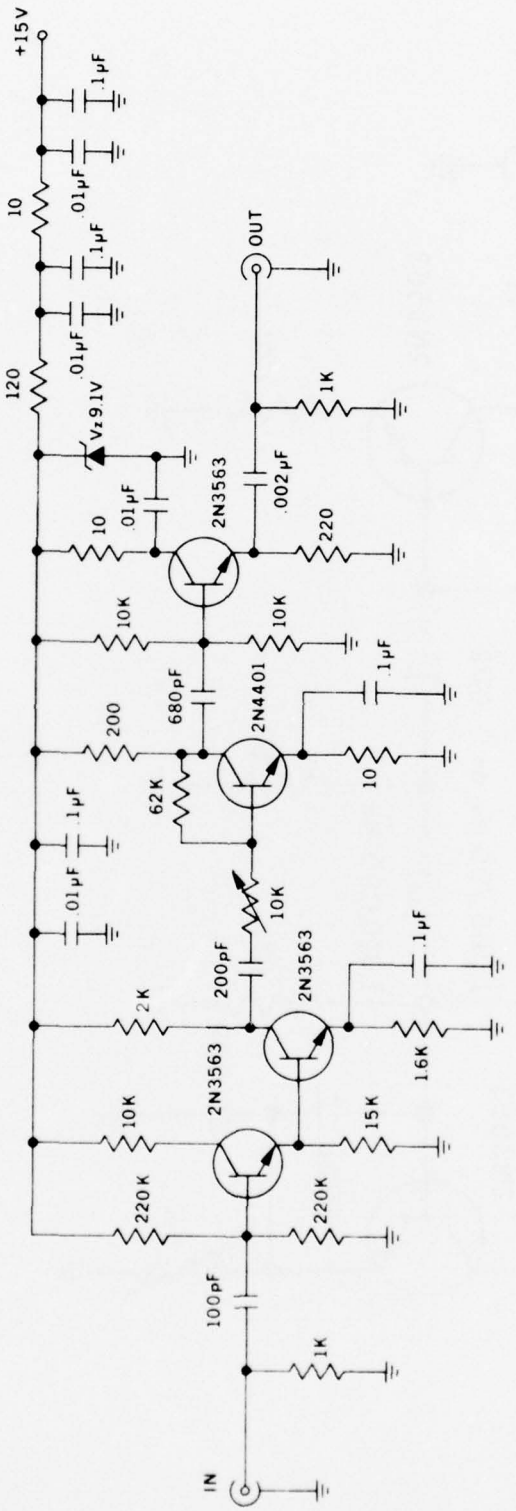

Figure B-4. Receiver Module

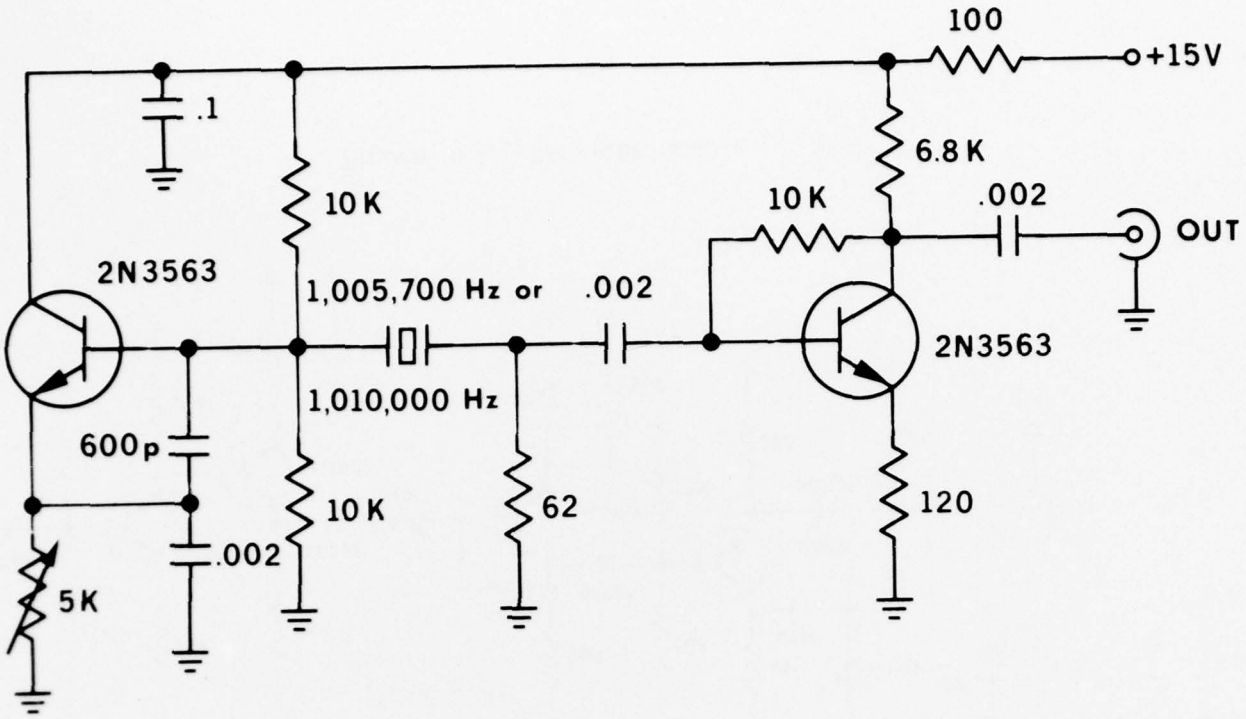

Figure B-5. Local Oscillator

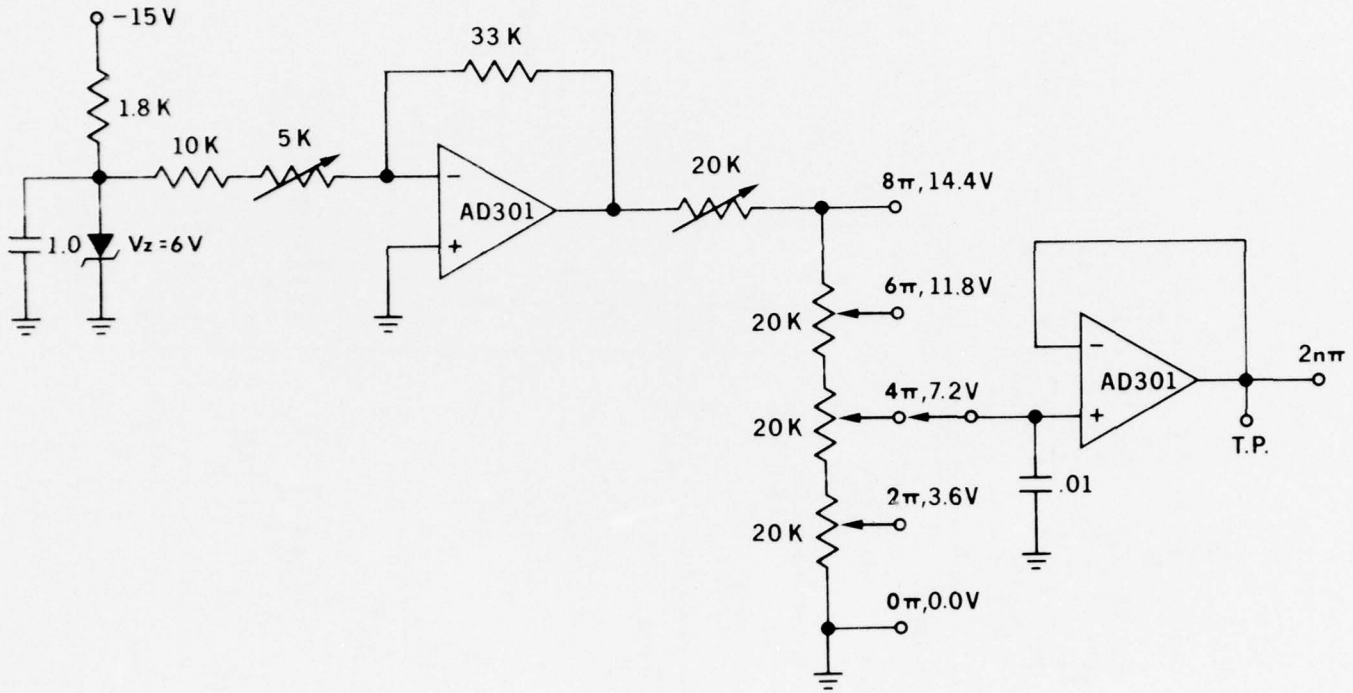

Figure B-6. Multiple Period Offset Generator

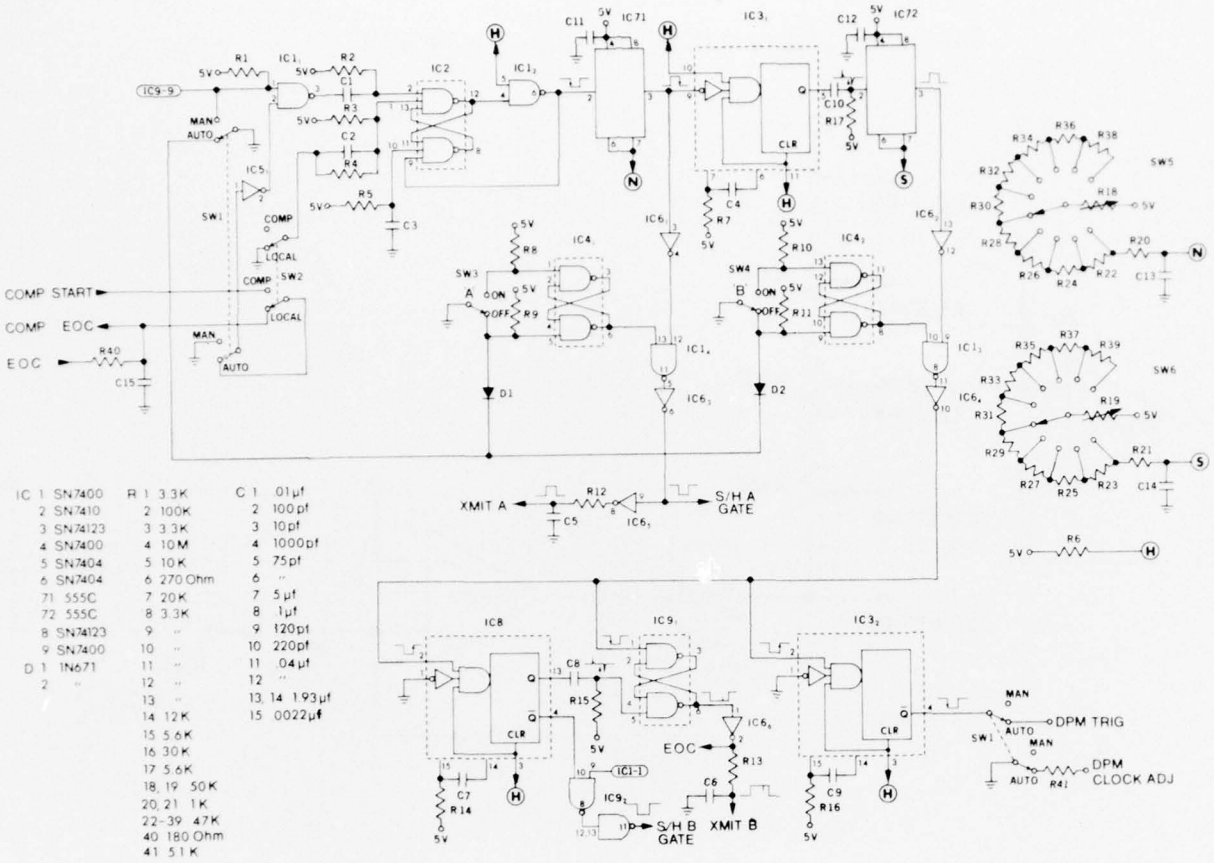

Figure B-7. Logic Circuit

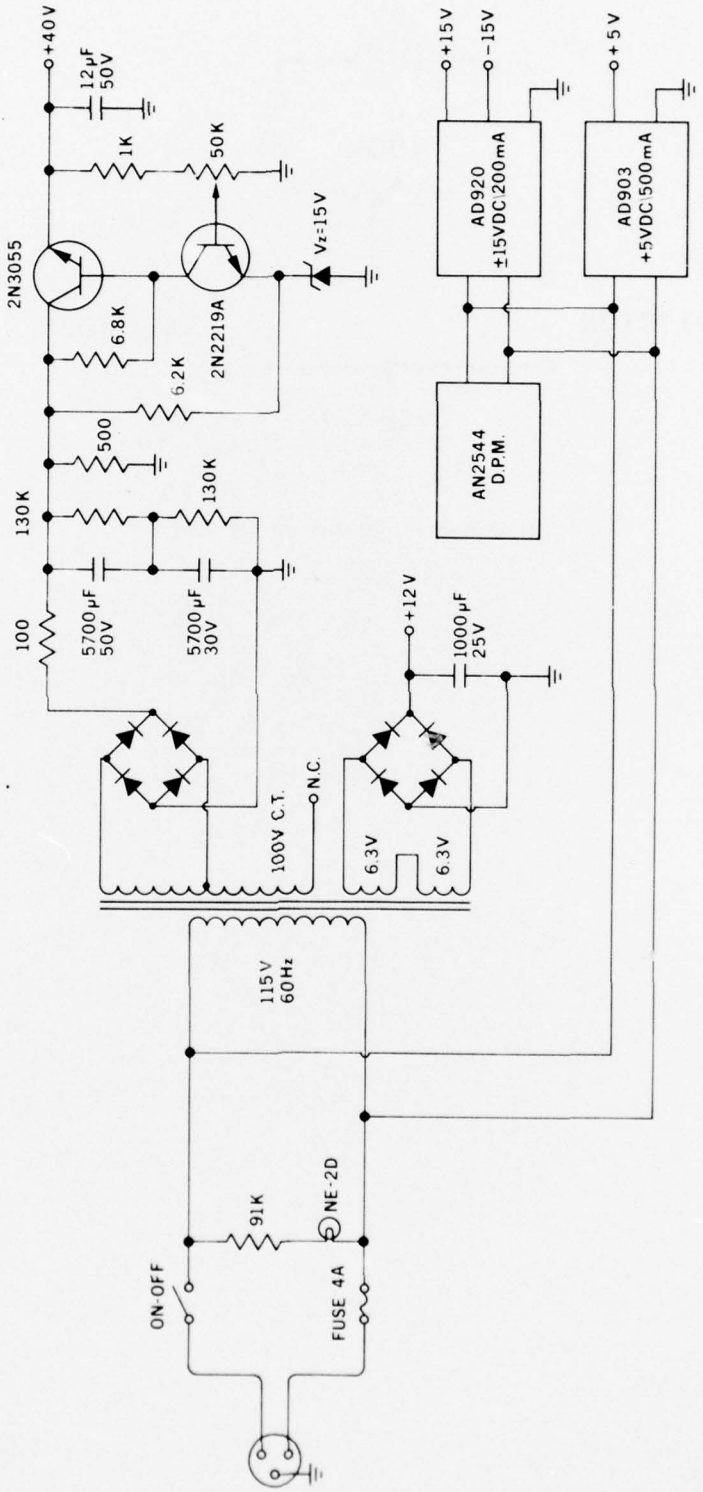

Figure B-8. Power Supply

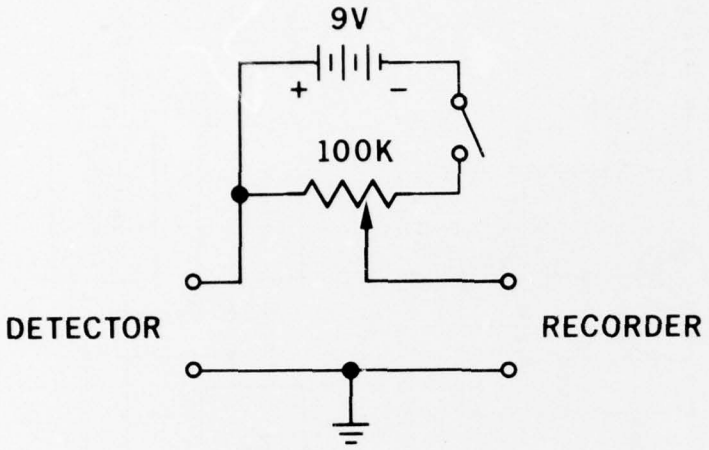

Figure B-9. Recorder Offset

INITIAL DISTRIBUTION

Hq USAF/PREE	1	AFCEC/SU	1
Hq USAF/PREVP	1	AFCEC/SUL	1
Hq USAF/PREVX	1	AFCEC/WE	1
Hq USAF/RDPS	2	AFCEC/EV	5
Hq USAF/SAFOI	1	AFCEC/EVD	1
Hq USAF/SGPA	2	AFCEC/EVC	1
AFLC/SGB	1		
AFSC/DEV	1		
AFSC/SGB	1		
AFSC/SGPE	1		
AFSC/DLCAM	2		
AFOSR (Life Sciences)	1		
AMRL/DAL	1		
AMRL/THE	1		
OEHL/CC	3		
OEHL/OL-AA	1		
OEHL/OL-AB	1		
AFWL/SUL	1		
AFGL/XOP	1		
USAFSAM/EDE	2		
AMD	1		
ADTC/CSV	1		
ADTC/DLOSL	1		
1035 USAF Tech Ops Gp/TDM	1		
1 Med Service Wg/SGB	1		
Univ of New Mexico/Dept of Chemistry	3		
DDC/TCA	12		
Def Resch & Engrg/AD (E&LS)	1		
OASD/I&L)ES	1		
USA WW Exp Sta	1		
USA CERL	1		
USA Eng R&D Lab/MERDC	1		
DARD-ARE-E	1		
NCEL/Code 25111	1		
Nav Ship R&D Ctr/Code 3021	1		
Technology Transfer Staff (EPA)	1		
Office of Rsch and Development	1		
National Science Foundation	1		
SGRD-UGB	1		
Stanford Univ/Dept of Civ Engrg	1		
Stanford Univ/Dept of Earth Sciences	1		
Calif Inst of Tech/Dept Env Sciences	1		
Mass Inst of Tech/Dept of Civ Engrg	1		
Toxic Matls Information Center	1		
Univ of New Mexico/Dept of Civ Engrg	1		
Southeast Environ Research Lab	1		
Pacific Northwest Environ Rsch Lab	1		

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